ANIMAL AND VEGETABLE

FIXED OILS, FATS, BUTTERS, AND WAXES:

THEIR PREPARATION AND PROPERTIES,

AND THE

Manufacture therefrom of Candles, Soaps, and other Products.

BY

C. R. ALDER WRIGHT,

D.Sc.(Lond.), B.Sc.(Vict.), F.R.S.

THIRD EDITION, REVISED AND GREATLY ENLARGED BY

C. AINSWORTH MITCHELL,

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PREFACE TO THE THIRD EDITION.

Dr. Alder Wright's book on Fixed Oils, Fats, Butters, and Waxes was the first complete scientific treatise on the subject, and has for many years been a standard work of reference. The revision for the second edition fitted it more particularly for use as an analytical text-book, and a very large edition was quickly exhausted. The war prevented earlier revision, and for two years the book has been out of print; meanwhile technical literature on the subject has multiplied, and books have been published on individual oils, such as linseed and cotton-seed oils, which in themselves are nearly as long as the first edition of this book.

In preparing the third edition, therefore, it has been necessary to make a selection from the mass of material available, if the book was not to become encyclopædic in its character, and I have consequently been largely guided in this respect by the aims of the author as expressed in his preface. In many respects his book is different from any other, and I have endeavoured to interfere as little as possible with that individuality, while incorporating new matter with the old. For this reason I have retained the details of many of Dr. Wright's original investigations, which may very well become the starting point of fresh processes in the future.

The section dealing with margarine has been re-written, and in this connection I would like to express my thanks to the Planters' Margarine Company for their kindness in placing information of processes at my disposal, and supplying diagrams of machinery. A new chapter on hydrogenated oils has been added, and I am greatly indebted to Mr. H. Lane for his assistance in this subject, and for permission to reproduce diagrams of his plant.

I gratefully acknowledge the assistance of the firms who have again placed at my disposal illustrations of their plant and apparatus. These include Messrs. Rose, Downs & Thompson, Messrs. Greenwood & Batley, Messrs. Neill & Sons, Messrs. E. Cowles & Co., Messrs. S. H. Johnson, and Messrs. Baird & Tatlock.

In the analytical portion of the book I have brought the methods up-to-date, and have selected the most important of the products which have come into prominence during the last few years to be included in the systematic description of oils and fats, which I introduced into the second edition.

While the book was in the press, reports on standard methods for sampling and examining commercial samples of vegetable fats and oils were issued by the Ministry of Food. Although these analytical methods make no pretentions to being complete, they are almost certain to be generally adopted as the basis of agreement between buyers and sellers, and are therefore included in full in an appendix.

The investigations of the last few months on the important subject of the so-called vitamines in relation to fats appeared too late to be included in the earlier part of the work, and have therefore been summarised in a second appendix.

In conclusion, it gives me pleasure to acknowledge the assistance I have received from Miss Elliott, M.B.E., in making technical drawings and abstracts and in the indexing of this book; and finally, I congratulate the publishers on the results of their efforts, for they have spared no expense that the work might continue to fulfil its useful purpose.

C. AINSWORTH MITCHELL.

White Cottage, The Common,
Amersham, Buckinghamshire.
October, 1920.

PREFACE TO THE FIRST EDITION.

THE complete discussion of the Sources, Production, and General Technology of the numerous substances included in the term *Oils*, and of the intimately associated *Fats*, *Butters*, and *Waxes* (all of which are practically oils when melted), would require far more space than is compatible with the limits of the present work; it has accordingly been found indispensable to make a selection from this wide field, as the result of which the subjects now dealt with are narrowed down to the Animal and Vegetable Fixed Oils and allied substances; whilst Mineral Oils, Products of Distillation, Essential Oils, and various analogous materials are only discussed in so far as they are associated with the Fixed Oils in their technological applications. For the same sufficient reason, minute details respecting the various special tests employed in the practical examination of oils, &c., for adulterations have, as a rule, been omitted; as also have the descriptions of the distinctive properties and qualities of the individual oils and fats, excepting in a comparatively small number of typical cases. In short, the object aimed at has rather been to give general descriptions of the methods whereby Animal and Vegetable Oils and Fat are obtained from natural sources, of their leading practical applications and uses, and of their chief physical and chemical properties and reactions, than to enter into special details, and to discuss minutely the analytical tests and processes applicable in each separate case for the detection of adulteration.

The literature relating to the chemistry and technology of fixed oils and fats is already voluminous, and yearly increases considerably in magnitude, being mostly dispersed throughout the pages of numerous scientific and technical serials. Amongst the periodicals of this description consulted for the purpose of gathering together to some extent these scattered results and items may be more particularly mentioned:—

The Journal of the Society of Chemical Industry.
The Journal of the Society of Arts.
The Journal of the Chemical Society.
The Analyst.
The Chemical News.
Zeitschrift für angewandte Chemie.
Berichte der deutschen Chemischen Gesellschaft.
Dingler's polytechnisches Journal.
Biedermann's Technisch-Chemisches Jahrbuch.
Moniteur Scientifique.
Bulletin de la Societé Chimique de Paris.
Comptes rendus.

Besides many others in which papers bearing on the matters in hand appear from time to time. Various text-books and technical dictionaries previously published in this country or abroad have also been freely consulted with the object of rendering the present work as complete as possible, with due regard to the limits of space. In particular, the author desires to express his indebtedness to the following works:—

Schädler, *Technologie der Fette und Oele.* Berlin, 1883.

Allen, *Commercial Organic Analysis*, vol. ii., Second Edition. London, 1886.

Schädler, *Untersuchungen der Fette und Oele* Leipzic, 1889.

Benedikt, *Analyse der Fette und Wachsarten*, Second Edition. Berlin, 1892.

To the firm of Rose, Downs & Thompson, of Hull, the author is greatly indebted for numerous illustrations of the most recent and effective forms of oil mill machinery, as well as for valuable information concerning their use in oil extraction generally. In similar fashion he desires to thank Messrs Neill & Sons, of St. Helens, for a variety of specially-made drawings of appliances used in soap manufacture; Messrs. S. H. Johnson, of Stratford, for drawings of the newest forms of filter presses; and Messrs. E. Cowles & Co., of Hounslow, for cuts of improved candle-making machines.

C. R. ALDER WRIGHT.

LONDON, *October*, 1893.

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§ 1. General Composition and Nature of Oils, Butters, Fats, Waxes, and Allied Substances.

CHAPTER I.

THE SOURCES AND GENERAL NATURE OF NATURAL AND ARTIFICIAL OILS, ETC.

AMONG the alchemists the term "oil" had a somewhat wider range of application than is usual at the present day, including various inorganic substances, such as "oil of vitriol." Similarly "butter of antimony" and "butter of tin" were metallic derivatives entirely dissimilar from cow's butter in constitution, although resembling it in physical consistency. Even when such wholly inorganic compounds are excluded, the term "oil" has still an extremely elastic meaning, being employed to designate a very large variety of liquid substances, natural and artificial, which have but few features in common beyond the fact that, being all organic in character, they are capable of burning with more or less facility under suitable conditions; whilst with but very few exceptions they are practically insoluble in water, so as to be incapable of permanent solution therein; being as a rule lighter than water, when agitated therewith an emulsion forms, from which the water and oil gradually separate on standing, the latter usually floating as a separate layer on the former.

The term "fatty matter," or more shortly "fat," is applied to substances which are more or less of a soft solid character at the ordinary temperature, but on gently heating pass to liquids closely resembling fluid oils in general characters; "butters" being specially soft varieties of such fats possessing the peculiar physical texture of cow's butter at the atmospheric temperature of temperate climates. "Waxes," on the other hand, possess a somewhat different and much firmer texture at the ordinary temperature, but when heated melt to fluids which closely resemble ordinary liquid oils and melted fats in their general physical characters.

Oils proper are derived from animal, vegetable, and mineral sources, being, for the most part, originally present in the tissues, seeds, or strata, etc., from which they are obtained by simple mechanical processes, such as pressure or pumping, or by means of solvents, or by volatilisation. Certain products of destructive distillation, however, are also ranked amongst oils—*e.g.*, the "light oils," "creosote oils," etc., obtained during the rectification of coal tar; and "shale oils," "bone oil" (Dippel's oil, or bone tar), "paraffin oils," "rosin oils," and similar substances formed by the breaking up of more complex organic matters under the influence of heat. Somewhat similar substances (fusel oils) are produced by analogous decompositions occurring during fermentative changes.

Oils capable of being converted into vapour by the application of heat without suffering material decomposition (*volatile oils*) are for the most part either artificial products of destructive distillation, natural mineral oils (petroleum, very probably formed underground by the long-continued action of intraterrestrial heat on subterranean organic matter), or "essential" oils—*i.e.*, volatile odorous matters extracted from numerous vegetable sources, usually by distillation with water. *Fixed oils*, on the other hand, are substances not volatile without decomposition, and are essentially of animal and vegetable origin; as also are butters, fats, and waxes (which practically become fixed oils on slightly raising the temperature), with the exception of the so-called waxes of mineral origin, paraffin wax, ozokerite, ceresin, etc.[1]

From the point of view of general chemical composition, oils, fats, butters, and waxes may be divided into two leading classes—viz., those consisting of carbon and hydrogen only (*hydrocarbons*); and those containing carbon, hydrogen, and oxygen. Oils, etc., of the former class are practically all volatile without decomposition; those of the second class are in some cases volatile without change (*e.g.*, oxidised essential oils), but, as a rule, are "fixed," undergoing destructive distillation when heated, so that the vapours emitted are produced in consequence of decomposition.

Hydrocarbon oils include a large number of "essential oils" (in which oxidised substances are often present with the hydrocarbons); paraffin and petroleum oils, including the lightest and most volatile distillates of the "benzoline" class, "burning oils" (kerosenes, etc.) of medium volatility, "lubricating oils" of higher boiling point, and paraffin waxes, etc.; coal-tar oils of various kinds; and other analogous products of destructive distillation, from which various "closed chain" hydrocarbons (benzene, naphthalene, anthracene, etc.) can be isolated, together with many other kinds of hydrocarbons, some of the "saturated" class (paraffins, indicated by the general formula C_nH_{2n+2}), some of the "unsaturated" classes (C_mH_{2n}, where n is not greater than m).

Oils that contain oxygen (including fats, butters, and waxes), from the point of view of chemical constitution, are divisible into two classes—viz., those that are, and those that are not, of the nature of "compound ethers," or substances capable of undergoing changes of the character of that known as "saponification." Oils of the first class are again divisible into two groups—viz., *Glycerides*, or oils, etc.,

---

[1] The terms "fat" and "butter" are not confined to the fatty matters obtainable from the adipose tissues of animals and the milk of mammalia. Thus, various vegetable fats and butters are known—*e.g.*, *Dika fat*, *Palm oil*, *Shea butter*, *vegetable tallow*, *etc.* Similarly, whilst animal waxes are the best known products of the wax class, various forms of vegetable wax occur in nature (*e.g.*, *Carnauba wax*).

developing glycerol by saponification; and *Non-glycerides*, or oils not developing glycerol by saponification, but giving rise instead to some other alcoholiform product. As examples of these two groups may be mentioned, olive oil, coconut oil, mutton tallow, cow's butter, Japan wax, linseed oil, colza oil, cod-liver oil, and whale oil, essentially glyceridic in character; and oil of wintergreen (chiefly methyl salicylate), beeswax (mainly myricyl palmitate), spermaceti (chiefly cetyl palmitate), and sperm and doegling oils, essentially non-glyceridic in character.

Oils, etc., of the second class (non-saponifiable) include various oxygenated essential oils belonging to different organic families—*e.g.*, *aldehydes*—such as oil of bitter almonds (benzoic aldehyde); *ketones*, like oil of rue (methyl-nonyl-ketone) and oil of tansy (methyl-octyl-ketone); *alcohols*, such as oil of geranium (geraniol); *camphor analogues*, such as oil of wormwood (absinthol); and *resinoid constituents*. Various alcoholiform substances are also contained in the free state in natural oils, greases, etc. Thus wool-grease contains *cholesterol*, and ambergris an allied body *ambreol;* whilst similar substances are found in small quantity in many vegetable oils. Higher alcohols (*e.g.*, *cetylic alcohol*) are often present in the free state in marine cetacean oils; whilst *phenol* and its homologues are present in coal-tar oils and other products of destructive distillation.

SAPONIFICATION.

Originally the term "Saponification" was used to designate the chemical changes taking place when soap is prepared by the action of alkalis on fixed oils and fats; but subsequently it has been extended to include a large number of parallel changes occurring where various classes of "compound ethers" are broken up under the influence of alkalis or other bases, so as to give rise, on the one hand, to the metallic salt of an organic acid, and, on the other, to an alcoholiform complementary product. The following equations represent typical reactions of saponification, in which the alcoholiform product is respectively an alcohol of the monohydric, dihydric, trihydric, or tetrahydric class:—

$$\begin{array}{lccccccc} & \text{Ethyl Acetate.} & & \begin{matrix}\text{Potassium}\\ \text{Hydroxide.}\end{matrix} & & \begin{matrix}\text{Potassium}\\ \text{Acetate.}\end{matrix} & & \begin{matrix}\text{Ethylic}\\ \text{Alcohol.}\end{matrix} \\ 1. & C_2H_5 . O . C_2H_3O & + & K . OH & = & K . O . C_2H_3O & + & C_2H_5 . OH \end{array}$$

$$\begin{array}{lccccccc} & \text{Ethylene Diacetate.} & & \begin{matrix}\text{Potassium}\\ \text{Hydroxide.}\end{matrix} & & \begin{matrix}\text{Potassium}\\ \text{Acetate.}\end{matrix} & & \text{Glycol.} \\ 2. & C_2H_4\left\{\begin{matrix} O . C_2H_3O \\ O . C_2H_3O \end{matrix}\right. & + & 2K . OH & = & 2K . O . C_2H_3O & + & C_2H_4\left\{\begin{matrix} OH \\ OH \end{matrix}\right. \end{array}$$

$$\begin{array}{lccccccc} & \begin{matrix}\text{Glyceryl Tristearate}\\ \text{(Stearin).}\end{matrix} & & \begin{matrix}\text{Sodium}\\ \text{Hydroxide.}\end{matrix} & & \begin{matrix}\text{Sodium}\\ \text{Stearate.}\end{matrix} & & \text{Glycerol.} \\ 3. & C_3H_5\left\{\begin{matrix} O . C_{18}H_{35}O \\ O . C_{18}H_{35}O \\ O . C_{18}H_{35}O \end{matrix}\right. & + & 3Na . OH & = & 3Na . O . C_{18}H_{35}O & + & C_3H_5\left\{\begin{matrix} OH \\ OH \\ OH \end{matrix}\right. \end{array}$$

$$\begin{array}{lccccccc} & \text{Erythrol Tetrabenzoate.} & & \begin{matrix}\text{Sodium}\\ \text{Hydroxide.}\end{matrix} & & \begin{matrix}\text{Sodium}\\ \text{Benzoate.}\end{matrix} & & \text{Erythrol.} \\ 4. & C_4H_6\left\{\begin{matrix} O . C_7H_5O \\ O . C_7H_5O \\ O . C_7H_5O \\ O . C_7H_5O \end{matrix}\right. & + & 4Na . OH & = & 4Na . O . C_7H_5O & + & C_4H_6\left\{\begin{matrix} OH \\ OH \\ OH \\ OH \end{matrix}\right. \end{array}$$

The majority of saponification changes occurring with natural fixed oils and fats, etc., belong to the third class—*i.e.*, these substances are chiefly "glycerides," or compound esters furnishing glycerol on saponification. Some liquid fixed saponifiable oils, however, are of non-glyceridic character, undergoing saponification changes of the first kind; thus sperm oil largely consists of *cetyl physetoleate* and homologous substances, broken up by saponification, thus—

$$\begin{array}{ccccccc} \text{Cetyl Physetoleate.} & & \text{Potassium Hydroxide.} & & \text{Potassium Physetoleate.} & & \text{Cetylic Alcohol.} \\ C_{16}H_{33} . O . C_{16}H_{29}O & + & K . OH & = & K . O . C_{16}H_{29}O & + & C_{16}H_{33} . OH \end{array}$$

Most waxes possess an analogous constitution. Thus the chief constituents of beeswax and spermaceti are respectively *myricyl palmitate* and *cetyl palmitate*, which are capable of being decomposed by saponification, thus—

$$\begin{array}{ccccccc} \text{Myricyl Palmitate.} & & \text{Sodium Hydroxide.} & & \text{Sodium Palmitate.} & & \text{Myricylic Alcohol.} \\ C_{30}H_{61} . O . C_{16}H_{31}O & + & Na . OH & = & Na . O . C_{16}H_{31}O & + & C_{30}H_{61} . OH \end{array}$$

$$\begin{array}{ccccccc} \text{Cetyl Palmitate.} & & \text{Potassium Hydroxide.} & & \text{Potassium Palmitate.} & & \text{Cetylic Alcohol.} \\ C_{16}H_{33} . O . C_{16}H_{31}O & + & K . OH & = & K . O . C_{16}H_{31}O & + & C_{16}H_{33} . OH \end{array}$$

Some few vegetable waxes, however, are of glyceridic character —*e.g.*, Japan wax, chiefly consisting of *palmitic triglyceride*, $C_3H_5(O . C_{16}H_{31}O)_3$.

A considerable number of oxidised essential oils also consists mainly of compound esters of the first class. Thus oil of winter-green (*Gaultheria procumbens*) mainly consists of *methyl salicylate*, and oil of cow parsnip (*Heracleum spondylium*) of *octyl acetate;* respectively saponified, thus—

$$\begin{array}{ccccccc} \text{Methyl Salicylate.} & & \text{Potassium Hydroxide.} & & \text{Potassium Salicylate.} & & \text{Methylic Alcohol.} \\ CH_3 . O . C_7H_5O_2 & + & K . OH & = & K . O . C_7H_5O_2 & + & CH_3 . OH \end{array}$$

$$\begin{array}{ccccccc} \text{Octyl Acetate.} & & \text{Sodium Hydroxide.} & & \text{Sodium Acetate.} & & \text{Octylic Alcohol.} \\ C_8H_{17} . O . C_2H_3O & + & Na . OH & = & Na . O . C_2H_3O & + & C_8H_{17} . OH \end{array}$$

Compound esters of Class II. (furnishing dihydric alcohols on saponification), although not absolutely unknown amongst natural products of the oil, fat, and wax class, are very rare; carnauba wax has been found to yield (*inter alia*) a glycol, $C_{25}H_{50}\left\{\begin{matrix}OH\\OH\end{matrix}\right.$, on saponification (p. 19). Tetrahydric esters, like those of erythrol, have not as yet been recognised as constituents of oils and fats, etc.; and the same remark applies to the yet more complex pentahydric and hexhydric esters; mannitol, $C_6H_8(OH)_6$, a hexhydric alcohol, has been found as a constituent of vegetable fruits, etc., accompanying oil—*e.g.*, in unripe olives; but neither mannitol nor any of its esters appear to be contained in purified expressed olive oil.

CLASSIFICATION OF OILS, FATS, WAXES, ETC., ACCORDING TO CHEMICAL COMPOSITION.

The following table indicates a rough classification of the principal varieties of oils, fats, and waxes in accordance with the general chemical character of their leading constituents :—

Division I.—Hydrocarbons.

1. Natural essential oils, mostly of vegetable origin.
2. Natural mineral oils (petroleum), including the crude oils, and the products thence obtained by distillation, etc. (benzoline, kerosene oils, lubricating oils, etc.).
3. Artificial products of destructive distillation (paraffin oils, shale oils, bone oils, coal-tar oils, etc.).
4. Solid hydrocarbons from natural products (earth-wax, etc.) or isolated from the two previous sources—*e.g.*, paraffin wax and allied substances largely used in candle-making.

Division II.—Containing Oxygen.

A.—Saponifiable.

1. *Essential compound esters of monohydric alcohols.*
    - *a.* Various natural essential oils mostly of vegetable origin.
    - *b.* Certain animal fixed oils, especially those of cetacean origin (sometimes termed "liquid waxes").
    - *c.* Most animal and vegetable solid waxes (waxes proper).
    - *d.* Certain artificial essential oils—*e.g.*, various compound esters used for perfumery and flavouring purposes.
2. *Essential glycerides, or compound esters of glycerol.*
    - *a.* The majority of animal and vegetable fixed oils, fats, and butters.
    - *b.* Some few vegetable waxes.

B.—Not Saponifiable.

- *a.* Various essential oils, consisting of aldehydes, ketones, camphoraceous bodies, etc.
- *b.* Alcoholiform constituents of natural animal and vegetable oils (cholesterol, phytosterol, cetylic alcohol, etc.).
- *c.* Alcoholiform bodies formed by fermentation (fusel oils).
- *d.* Phenoloid bodies formed by destructive distillation and contained in coal-tar, etc. (phenol, cresol, etc.).
- *e.* Products formed by oxidation of hydrocarbons—*e.g.*, "Sanitas oil" (formed by the atmospheric oxidation of oil of turpentine).

In the present work a large number of the various substances thus coming into the general category of oils, fats, butters, and waxes is necessarily excluded from minute consideration, fixed animal and vegetable oils and fats, etc., all practically belonging to Division II., Sections 1 and 2. Certain hydrocarbons, however, are intimately connected with the subjects dealt with, more especially mineral oils and products of destructive distillation employed as adulterants of animal and vegetable fixed oils, and as ingredients in lubricating mixtures, etc.; and mineral waxes (paraffin wax, ozokerite, and similar substances) employed as candle materials. Various essential oils, moreover, are in use as ingredients in certain kinds of fancy (toilet) soaps as perfuming agents, and in some kinds of sanitary soaps (*e.g.*, eucalyptus oil); as also are certain products of destructive distillation (*e.g.*, carbolic acid and its higher homologues).

For further classifications of fixed oils, fats, waxes, etc. (apart from other kinds of oils), based either on their physical characters and the chemical nature of their main ingredients, or on their leading technical uses, *vide* Chapter XIII.

CHAPTER II.

SAPONIFICATION PRODUCTS OF OILS, FATS, WAXES, ETC.

ALCOHOLIFORM PRODUCTS.

A saponifiable oil, etc., as above stated, gives rise to two products under the influence of alkalis—viz., an alcoholiform organic substance (which in practice is either glycerol or some kind of monohydric alcohol), and the alkali salt of an organic acid. Under suitable conditions (more especially heating under pressure in contact with water) parallel decompositions can be brought about by means of water, the products of the "hydrolysis" thus effected being the alcoholiform body and a free "fatty acid." Thus, in the cases of the glyceride of oleic acid and of cetyl palmitate, the hydrolytic actions take place in accordance with the following equations:—

$$\underset{\text{Oleic Glyceride.}}{C_3H_5\left\{\begin{array}{l} O\,.\,C_{18}H_{33}O \\ O\,.\,C_{18}H_{33}O \\ O\,.\,C_{18}H_{33}O \end{array}\right.} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Oleic Acid.}}{3C_{18}H_{33}O\,.\,OH} + \underset{\text{Glycerol,}}{C_3H_5\left\{\begin{array}{l} OH \\ OH \\ OH \end{array}\right.}$$

$$\underset{\text{Cetyl Palmitate.}}{C_{16}H_{33}\,.\,O\,.\,C_{16}H_{31}O} + \underset{\text{Water.}}{H_2O} = \underset{\text{Palmitic Acid.}}{C_{16}H_{31}O\,.\,OH} + \underset{\text{Cetylic Alcohol.}}{C_{16}H_{33}\,.\,OH}$$

Similar reactions occur in many other parallel cases, the nature of the alcoholiform body and of the fatty acid developed only differing in each instance.

TRIHYDRIC ALCOHOLS FORMED BY SAPONIFICATION (GLYCEROL).

Glycerol, the most frequently occurring alcoholiform saponification product of fixed oils and fatty matters, solidifies, when pure, to a crystalline mass by long continued chilling,[1] the melting point being about + 22° C.; its great hygroscopic character renders it extremely difficult to obtain absolutely free from water, in consequence of which values varying from 1·262 to 1·2653 have been stated as its specific gravity at 15° C. When heated gently under the ordinary atmospheric

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[1] Passing a few bubbles of chlorine into concentrated glycerol will often make it crystallise (*Werner*). Chilled glycerol usually crystallises when stirred up with a few crystals of the previously solidified substance, a method utilised in manufacture (Chap. xxii.).

pressure it volatilises without decomposition, but at higher temperatures splits up into water and *acrolein*, thus—

$$\underset{\text{Glycerol.}}{C_3H_8O_3} = 2H_2O + \underset{\text{Acrolein.}}{C_3H_4O}$$

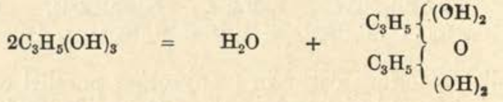
When heated *in vacuo* it boils at about 180° C.

By cautious oxidation with alkaline permanganate it yields oxalic acid in sufficiently accurate proportions for quantitative estimation. In like manner by treatment with potassium bichromate and sulphuric acid it forms carbon dioxide and water. When treated with acetic anhydride it forms triacetin, the saponification of which furnishes another means of quantitative determination (*vide* Chap. XXII.). In the absence of substances carbonised by sulphuric acid, an excellent qualitative test is to heat cautiously to 120° C. or a little higher a mixture of two drops of glycerol, two of fused phenol, and about as much sulphuric acid; a brown solid mass forms, which after cooling dissolves in ammonium hydroxide yielding a beautiful carmine red solution (*Reichl*). If substances that are carbonised are present they produce a dark brown colouring matter which hides the red tint.

Polyglycerols.—Glycerol heated in contact with hydrochloric acid or certain other dehydrating substances is capable of undergoing reactions of dehydration and condensation, which may be expressed by the general equation:—

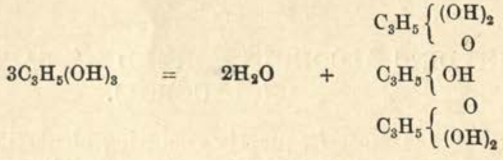
$$nC_3H_8O_3 = mH_2O + C_{3n}H_{8n-2m}O_{3n-m}$$

Thus when $n = 2$ and $m = 1$, *diglycerol* results.



$$2C_3H_5(OH)_3 = H_2O + \begin{array}{l} C_3H_5\left\{\begin{array}{l}(OH)_2\\ \end{array}\right. \\ \qquad O \\ C_3H_5\left\{\begin{array}{l} \\ (OH)_2\end{array}\right. \end{array}$$

And when $n = 3$ and $m = 2$, *triglycerol* is produced.



$$3C_3H_5(OH)_3 = 2H_2O + \begin{array}{l} C_3H_5\left\{\begin{array}{l}(OH)_2\\ O\end{array}\right. \\ C_3H_5\left\{OH\right. \\ C_3H_5\left\{\begin{array}{l}O\\ (OH)_2\end{array}\right. \end{array}$$

It has been supposed by some chemists that bodies of this class are sometimes contained in commercial "glycerins," more especially those formed under high pressure in autoclaves, or purified by distillation; such glycerin, when slowly evaporated at a temperature of about 160° C.,[1] leaves a non-volatile organic residue from the weight of which (after deducting ash) the proportion of polyglycerols present may be deduced. It does not appear, however, that the residue thus left has been definitely proved to have the character and composition

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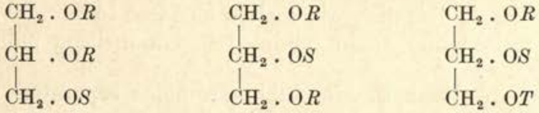
[1] Lewkowitsch, *Year Book of Pharmacy*, 1890, 380.

assigned to it, although the formation of polyglycerols is, *a priori*, highly probable.

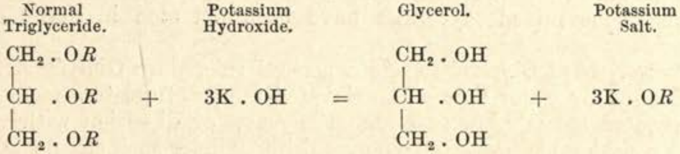
Natural Triglycerides.—At one time it was commonly accepted that as a general rule *only one acid radicle* was contained in any given glyceride; *i.e.*, that substances of the type



$$\begin{array}{l} CH_2 . OR \\ | \\ CH\ . OR \\ | \\ CH_2 . OS \end{array} \qquad \begin{array}{l} CH_2 . OR \\ | \\ CH_2 . OS \\ | \\ CH_2 . OR \end{array} \qquad \begin{array}{l} CH_2 . OR \\ | \\ CH_2 . OS \\ | \\ CH_2 . OT \end{array}$$

(where *R*, *S*, and *T* represent different radicles) were rarely met with.

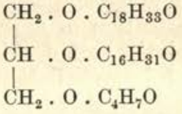
Evidence offered in support of the view that the original substance was a mixture of two or more triglycerides of the ordinary type (*i.e.*, containing only one acid radicle), was that on chilling an oil yielding palmitic and oleic acids on saponification, a solid fat usually separated, yielding only palmitic acid on saponification; whilst the liquid portion was substantially olein, the reaction in each case being represented by the general equation—



$$\begin{array}{ccccccc} \text{Normal Triglyceride.} & & \text{Potassium Hydroxide.} & & \text{Glycerol.} & & \text{Potassium Salt.} \\ \begin{array}{l} CH_2 . OR \\ | \\ CH\ . OR \\ | \\ CH_2 . OR \end{array} & + & 3K . OH & = & \begin{array}{l} CH_2 . OH \\ | \\ CH\ . OH \\ | \\ CH_2 . OH \end{array} & + & 3K . OR \end{array}$$

Natural Mixed Glycerides.—It has been shown, however, that in certain cases, at all events, mixed glycerides, in which the acid radicles are not all of the same kind, do exist in natural fats.

Cow's Butter.—There appears to be but little doubt as to the existence of a mixed glyceride in cow's butter. Although, on saponification, it yields butyric acid, no butyrin (triglyceride of butyric acid) can be dissolved out from it by means of alcohol; whereas artificial mixtures of butyrin and other triglycerides readily yield the former to that solvent. Hence the conclusion has been arrived at, that a mixed glyceride, *oleo-palmito-butyric glyceride*,[1]



$$\begin{array}{l} CH_2 . O . C_{18}H_{33}O \\ | \\ CH\ . O . C_{16}H_{31}O \\ | \\ CH_2 . O . C_4H_7O \end{array}$$

(or some analogous substance) is present, which breaks up on saponification with the formation of salts of oleic, palmitic, and butyric acids.

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[1] Blyth and Robertson, *Proc. Chem. Soc.*, 1889, 5.

Evidence of the existence of a mixed glyceride in butter fat has also been obtained in a different way by *Henriques* and *Künne* (*vide infra*).

Heise[1] isolated a mixed glyceride containing two radicles of stearic acid and one of oleic acid from the fat from the seeds of the East African tallow tree, and his results were subsequently confirmed by *Henriques* and *Künne*.[2] This oleo-distearin melted at 44·5° to 45·5° C., and after being once melted and again solidified had a melting point of 41·5° to 42·5° C.

It is probable that the insoluble bromides separated by *Hehner* and *Mitchell*[3] from linseed and fish oils are compounds of mixed glycerides containing linolenic acid (or other highly unsaturated fatty acid) and oleic acid (or other unsaturated fatty acid). (See *Linseed Oil.*)

The mixed glycerides of palmitic and stearic acids have been isolated from beef and mutton fats and from lard. *Bömer*[4] found that the most insoluble glyceride in lard was a palmito-distearin which melted at 68·5° and 51·5° C., and differed in its crystalline form from the isomeric palmito-distearin of mutton fat. Polenske's method of detecting beef and mutton fat in lard (see *Lard*) depends upon the presence of the different mixed glycerides in the fats.

Analogous mixed glycerides have been detected in many other fats.

Hydrolysis of Glycerides.—As a general rule, pure triglycerides are acted upon by water only at an elevated temperature, treatment with superheated steam blown through the mass, or digestion with water under considerable pressure being requisite. Under such circumstances, the glycerol set free is often more or less decomposed by secondary reactions. With crude unpurified oils continued standing at the ordinary temperature often suffices, the action in such cases being largely due to changes of a fermentative character taking place in the mucilaginous or albuminous extractive matters present as impurities; in extreme cases the action proceeds to such an extent as to hydrolyse the larger portion of the glycerides present, so that upwards of 50 per cent. of the mass is free fatty acid. Changes of this description are almost invariably accompanied by the production of bye-products of unpleasant taste and smell, so that the development of "rancidity" by this action greatly deteriorates the value of the oil, more especially for culinary and edible purposes.

In all probability the formation of a free fatty acid and glycerol from a glyceride by hydrolytic action takes place in three stages, giving rise to two kinds of intermediate products, *diglycerides* and *monoglycerides* respectively. Thus, if R be a fatty acid radicle—

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[1] *Arbeit. Kaiserl. Gesundheitsamt*, 1896, 540.

[2] *Ber.*, 1899, xxxii., 387.

[3] *Analyst*, 1898, xxiii., 317.

[4] *Zeit. Nahr. Genussm.*, 1913, xxv., 321.

$$\begin{array}{ccccccc}
\text{Normal Triglyceride.} & & \text{Water.} & & \text{Fatty Diglyceride.} & & \text{Fatty Acid.}\\
\mathrm{CH_2 . O}R & & & & \mathrm{CH_2 . O}R & & \\
| & & & & | & & \\
\mathrm{CH\ . O}R & + & \mathrm{H_2O} & = & \mathrm{CH\ . O}R & + & \mathrm{H . O}R\\
| & & & & | & & \\
\mathrm{CH_2 . O}R & & & & \mathrm{CH_2 . OH} & &
\end{array}$$

$$\begin{array}{ccccccc}
\text{Diglyceride.} & & \text{Water.} & & \text{Monoglyceride.} & & \text{Fatty Acid.}\\
\mathrm{CH_2 . O}R & & & & \mathrm{CH_2 . O}R & & \\
| & & & & | & & \\
\mathrm{CH\ . O}R & + & \mathrm{H_2O} & = & \mathrm{CH\ . OH} & + & \mathrm{H . O}R\\
| & & & & | & & \\
\mathrm{CH_2 . OH} & & & & \mathrm{CH_2 . OH} & &
\end{array}$$

$$\begin{array}{ccccccc}
\text{Monoglyceride.} & & \text{Water.} & & \text{Glycerol.} & & \text{Fatty Acid.}\\
\mathrm{CH_2 . O}R & & & & \mathrm{CH_2 . OH} & & \\
| & & & & | & & \\
\mathrm{CH\ . OH} & + & \mathrm{H_2O} & = & \mathrm{CH\ . OH} & + & \mathrm{H . O}R\\
| & & & & | & & \\
\mathrm{CH_2\ OH} & & & & \mathrm{CH_2 . OH} & &
\end{array}$$

The final action may consequently be expressed by the equation—

$$\begin{array}{ccccccc}
\text{Triglyceride.} & & \text{Water.} & & \text{Glycerol.} & & \text{Fatty Acid.}\\
\mathrm{CH_2 . O}R & & & & \mathrm{CH_2 . OH} & & \\
\mathrm{CH\ . O}R & + & \mathrm{3H_2O} & = & \mathrm{CH\ . OH} & + & \mathrm{3H . O}R\\
\mathrm{CH_2 . O}R & & & & \mathrm{CH_2 . OH} & &
\end{array}$$

which may be written somewhat more compactly—

$$\left.\begin{matrix}\mathrm{C_3H_5}\\ R_3\end{matrix}\right\}\mathrm{O_3} \quad + \quad \mathrm{3H_2O} \quad = \quad \left.\begin{matrix}\mathrm{C_3H_5}\\ \mathrm{H_3}\end{matrix}\right\}\mathrm{O_3} + \mathrm{3H . O}R$$

The formation of the intermediate substances by gradual hydrolysis has not been much studied as yet; in the case of rape oil, however, it has been shown that whilst fresh oil contains the triglyceride *erucin*,

$$\left.\begin{matrix}\mathrm{C_3H_5}\\ \mathrm{(C_{22}H_{41}O)_3}\end{matrix}\right\}\mathrm{O_3},$$

the corresponding diglyceride *dierucin*,

$$\left.\begin{matrix}\mathrm{C_3H}\\ \mathrm{(C_{22}H_{41}O)_2}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O_3} \quad = \quad \begin{matrix}\mathrm{CH_2 . O . C_{22}H_{41}O}\\ \mathrm{CH\ . O . C_{22}H_{41}O}\\ \mathrm{CH_2 . O . H}\end{matrix}$$

is sometimes contained in old oil,[1] probably formed as above by partial hydrolysis.

Synthesis of Glycerides.—On the other hand, the reverse reactions leading to the successive building up from glycerol of monoglyceride, diglyceride, and triglyceride are well known laboratory operations, thus—

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[1] Reimer and Will (*Ber.*, 1886, xix., 3320) found that a deposit which had slowly formed in a quantity of colza oil was not the triglyceride usually obtained under such conditions, but the diglyceride melting at 47° C.

Glycerol. Fatty Acid. Monoglyceride.

$$C_3H_5\left\{\begin{array}{l}OH\\OH\\OH\end{array}\right. + H.OR = C_3H_5\left\{\begin{array}{l}OR\\OH\\OH\end{array}\right. + H_2O$$

Monoglyceride. Diglyceride.

$$C_3H_5\left\{\begin{array}{l}OR\\OH\\OH\end{array}\right. + H.OR = C_3H_5\left\{\begin{array}{l}OR\\OR\\OH\end{array}\right. + H_2O$$

Diglyceride. Triglyceride.

$$C_3H_5\left\{\begin{array}{l}OR\\OR\\OH\end{array}\right. + H.OR = C_3H_5\left\{\begin{array}{l}OR\\OR\\OR\end{array}\right. + H_2O$$

In many cases, when it is desired to obtain triglycerides in a state of purity, it is more easy to saponify an oil, separate and purify the resulting fatty acids, and convert them into glycerides in this way than it is to separate the original glycerides themselves contained in the oil.

Properties of Pure Triglycerides.—The following boiling and melting points are possessed by some pure triglycerides prepared synthetically in this way :—

		Melting Point. °C.	Boiling Point. °C.
Butyrin, . .	$C_3H_5(O.C_4H_7O)_3$	Fluid	285
Laurin, . .	$C_3H_5(O.C_{12}H_{23}O)_3$	45	..
Myristin, . .	$C_3H_5(O.C_{14}H_{27}O)_3$	55	..
Palmitin, . .	$C_3H_5(O.C_{16}H_{31}O)_3$	62	..
Stearin, . .	$C_3H_5(O\ C_{18}H_{35}O)_3$	71·5	..
Olein, . . .	$C_3H_5(O.C_{18}H_{33}O)_3$	solidifies at −6° C	..

Free Acids in Hydrolysed Oils.—When oils that have become hydrolysed through rancidity are refined by treatment with alkalis (Chap. XI.), the free acids are removed and neutral oils left; but other kinds of refining processes do not affect the free acids, which accordingly are apt to be found in commecrial oils to varying extents, sometimes only inconsiderable amounts, and sometimes very large percentages being present. According to Thum the free acids do not consist solely of oleic acid, as is often supposed, but of a mixture in exactly the same proportions as that in which they exist in the undecomposed glycerides. Thus, palm oil and olive kernel oil containing much free acid yield as much solid free acids relatively to oleic acid when the free acids are removed by agitation with a cold alkaline lye, as are yielded by the neutral unsaponified fats present.

Just as the glyceridic compound esters of fatty acids are apt to be hydrolysed under appropriate conditions, so are their alkali salts (soaps) split up by water with the formation of basic substance (free alkali) and an acid salt (*vide* p. 24).

It is a remarkable fact that although a somewhat considerable number of monohydric alcohols is known to be formed by the saponification of fixed oils, essential oils, and similar substances, only one trihydric alcohol, viz., glycerol, has ever been found to be produced from such sources.

Theory of Saponification with Alkali.—*Geitel*[1] came to the conclusion, from mathematical and physical considerations, that during the saponification of triglycerides with alkali, mono- and di-glycerides were produced. *Henriques*[2] urged against this view the fact that, on partially saponifying almond oil with an insufficient quantity of alcoholic potassium hydroxide to liberate all the glycerol, he was only able to detect unaltered triglycerides in the unsaponified residue. He considered that Geitel's conclusion was unsupported by experimental evidence. Subsequently *Lewkowitsch*[3] demonstrated the correctness of Geitel's theory. He argued that, if the saponification produced only glycerol and fatty acids, the acetyl value (*q.v.*) of the partially saponified fat should not exceed that of the original fat; but that if, on the other hand, lower glycerides were formed as intermediate products, these, having a definite acetyl value, would cause an increase in the acetyl value of the sample. Confirmatory evidence would also be obtained from the Hehner and saponification values of the acetylated products, which would show great variations in the presence of mono- or di-glycerides.

In the experiments several pounds of tallow and of cotton-seed oil were saponified with sodium or calcium hydroxides, as in the ordinary manufacturing process. From time to time samples were withdrawn, treated with hydrochloric acid, washed, and dried. The acetyl, the Hehner, and saponification values of the acetylated products were determined, whilst the amount of free acid calculated from the acid value showed to what extent the saponification had progressed.

It was found that the acetyl values rose and fell with the progress of the saponification, whilst at the same time the Hehner and saponification values of the acetylated products showed a corresponding variation.

Lewkowitsch points out that in such experiments as these only the mean values of the concurring phases of the saponification are determined, since simultaneously a molecule of diglyceride may be converted into monoglyceride and fatty acids, or a molecule of monoglyceride into fatty acids and glycerol, whilst a molecule of triglyceride is only passing through the first stage.

In one of Lewkowitsch's experiments the saponification proceeded with such rapidity that, but for the fact that a higher acetyl value was obtained with one of the first samples, the results might have appeared to support the older view of saponification.

Saponification with Alcoholic Alkali.—In addition to the formation of mono- and di-glycerides, the ethyl esters of the respective fatty acids present are formed as intermediate products during the saponification of triglycerides with alcoholic alkali. This was first observed by *Bouisin*[4] in 1857, and subsequently demonstrated by *Henriques*,[5] who fractionally saponified various oils with an insufficient proportion

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[1] *J. prakt. Chem.*, 1897, 429; 1898, 113.

[2] *Zeit. angew. Chem.*, 1898, 697.

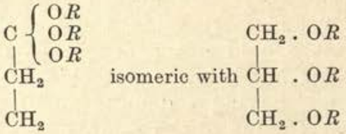
[3] *Ber.*, 1900, xxxii., 89.

[4] *Comptes Rendus*, xlv., 35.

[5] *Zeit. angew. Chem.*, 1898, 338.

of alcoholic potassium hydroxide, and in many cases separated the esters by distillation in a current of steam.

Isoglyceride Theory.—Theoretically the existence is possible of various substances possessing the composition of a trihydroxylated propane, $C_3H_5(OH)_3$, without being identical with glycerol. These substances would naturally form compound esters isomeric with ordinary glycerides containing the same acid radicles. Among such hypothetical bodies, the compound esters of *orthopropionic acid*, indicated by the general formula—



$$\begin{array}{l} C\left\{\begin{array}{l} OR \\ OR \\ OR \end{array}\right. \\ | \\ CH_2 \\ | \\ CH_2 \end{array} \quad \text{isomeric with} \quad \begin{array}{l} CH_2 . OR \\ | \\ CH \;\; . OR \\ | \\ CH_2 . OR \end{array}$$

have been supposed by some chemists to be present in certain fatty matters, notably cow's butter; but the experimental proofs of this supposition are singularly wanting in clearness and cogency. Such compound esters on saponification should neutralise four instead of three equivalents of alkali, generating an alkali propionate instead of glycerol; thus—

$$\overset{\substack{\text{Hypothetical} \\ \text{Isoglyceride.}}}{C_2H_5 . C(OR)_3} + \overset{\substack{\text{Sodium} \\ \text{Hydroxide.}}}{4NaOH} = \overset{\text{Sodium Propionate.}}{C_2H_5 . CO . ONa} + \overset{\text{Sodium Salt.}}{3NaOR} + \overset{\text{Water.}}{2H_2O}$$

MONOHYDRIC ALCOHOLS FORMED BY SAPONIFICATION.

Numerous groups of alcohols (monohydroxylated hydrocarbons) are known to the chemist, derived successively from saturated hydrocarbons of the series $C_n H_{2n+2}$, and from the other series of hydrocarbons containing less hydrogen, by the replacement of hydrogen by hydroxyl. Thus, *inter alia*, the following families of alcohols are known:—

Ethylic alcohol homologues ; general formula, $C_n H_{2n+1} . OH$
Allylic ,, ,, ,, ,, $C_n H_{2n-1} . OH$
Phenol ,, ,, ,, $C_n H_{2n-7} . OH$
Cinnamic alcohol ,, ,, ,, $C_n H_{2n-9} . OH$

Although representatives of several such groups of alcohols are found amongst products of destructive distillation (coal-tar oils, etc.), and in essential oils and the allied balsams and other aromatic bodies, and in small quantities as natural constituents of fixed oils of various kinds (occurring there in the free state), yet compound ethers derived from alcohols of the first and second of the above groups appear to be the only kinds naturally occurring in fixed oils and waxes, etc.; and of these by far the most frequently occurring substances belong to the first class.

Name.	Formula.	Boiling Point.	Melting Point.	Sources.
Methylic alcohol,	$CH_3 . OH$	66° C.	...	Saponification of oil of wintergreen; wood distillation products.
Ethylic alcohol,	$C_2H_5 . OH$	78°	...	Fermentation of saccharine matter.
Propylic alcohol,	$C_3H_7 . OH$	97°	...	Fermentation fusel oils.
Isopropylic alcohol,		84°	...	Isopropylic iodide from glycerol and hydriodic acid.
Normal Butylic alcohol,	$C_4H_9 . OH$	117°	...	Heavy oils from brandy.
Isobutylic alcohol		107°	...	Potato and beet fusel oils.
Amylic alcohols (several isomeric modifications),	$C_5H_{11} . OH$	127°-138°	...	Fusel oils from grain spirit, &c. Saponification of oil of Roman chamomile.
Hexylic alcohols (several modifications),	$C_6H_{13} . OH$	147°-157°	...	Saponification of oil of cow's parsley, oil of Roman chamomile, &c.
Normal Primary Heptylic alcohol,	$C_7H_{15} . OH$	176°	...	Brandy fusel oils. Hydrogenation of œnanthol from castor oil.
Octylic alcohols,	$C_8H_{17} . OH$	180°-192°	...	Saponification of oil of *Heracleum spondylium* and *H. giganteum*. Action of hot alkali on castor oil.
Nonylic alcohols,	$C_9H_{19} . OH$	...	...	... ...
Normal Primary Decylic alcohol,	$C_{10}H_{21} . OH$	119° at 15 millims. pressure.	7° C.	Hydrogenation of capric aldehyde.
Secondary Hendecylic alcohol,	$C_{11}H_{23} . OH$	229°	...	Hydrogenation of oil of rue.
Dodecylic alcohols,	$C_{12}H_{25} . OH$	143° at 15 millims. pressure.	24°	Hydrogenation of lauric aldehyde.
Tridecylic alcohols,	$C_{13}H_{27} . OH$	...	19°	Saponification of sperm oil.
Normal Primary Tetradecylic alcohol,	$C_{14}H_{29} . OH$	167° at 15 millims. pressure.	38°	Hydrogenation of myristic aldehyde.
Pentadecylic alcohols,	$C_{15}H_{31} . OH$	...	...	... ...
Normal Primary Hexadecylic alcohol,	$C_{16}H_{33} . OH$	189·5° at 15 millims. pressure.	49·5°	Hydrogenation of palmitic aldehyde.
Cetylic alcohol,		188°-193° at 15 mm. pressure.	49·2° ...	Saponification of spermaceti.
Heptadecylic alcohols,	$C_{17}H_{35} . OH$	...	...	... ...
Normal Primary Octodecylic alcohol,	$C_{18}H_{37} . OH$	210·5° at 15 millims. pressure.	59°	Hydrogenation of stearic aldehyde. Saponification of spermaceti (in small quantity).
Cerylic alcohol,	$C_{27}H_{55} . OH$	...	79°	Chinese wax.
Isocerylic alcohol,			62°	Carnauba wax. Wax of *Ficus gummiflua*.
Myricylic alcohol,	$C_{30}H_{61} . OH$	...	85°	Beeswax.
Isomyricylic alcohol?			72°	Carnauba wax.

ETHYLIC SERIES OF ALCOHOLS.

The table on p. 15 indicates the leading alcohols of this group (general formula $C_n H_{2n+1} . OH$) derived from fixed and essential oils and similar sources. In addition to those mentioned numerous isomeric modifications of many of them exist, and have been prepared by laboratory reactions.

The higher alcohols of this series, when fused with alkalis, evolve hydrogen with formation of the alkali salt of the corresponding fatty acid.[1] Thus—

Cetylic Alcohol.				Potassium Palmitate.		
$C_{15}H_{31} . CH_2 . OH$	+	KOH	=	$C_{15}H_{31} . CO . OK$	+	$2H_2$
Myricylic Alcohol.				Potassium Melissate.		
$C_{29}H_{59} . CH_2 . OH$	+	KOH	=	$C_{29}H_{59} . CO . OK$	+	$2H_2$

They are readily converted into compound esters by treatment with organic anhydrides (*e.g.*, acetic anhydride), and in some cases by heating with the acids alone, water being evolved.

Cetylic Alcohol.		Acetic Anhydride.		Cetyl Acetate.		Acetic Acid.
$C_{16}H_{33} . OH$	+	$(C_2H_3O)_2O$	=	$C_{16}H_{33} . O . C_2H_3O$	+	$C_2H_3O . OH$
Cetylic Alcohol.		Acetic Acid.		Cetyl Acetate.		Water.
$C_{16}H_{33} . OH$	+	$C_2H_3O . OH$	=	$C_{16}H_{33} . O . C_2H_3O$	+	H_2O

The compound esters thus produced are, in turn, readily saponified by alcoholic potassium hydroxide, and from the amount of alkali neutralised during the operation the molecular weight of the alcohol can be deduced, due corrections being made for unsaponifiable substances, etc., if present (Chap. VIII.).

ALLYLIC SERIES OF ALCOHOLS.

Alcohols of the series $C_n H_{2n-1} . OH$, derived from the olefine family of hydrocarbons of formula $C_n H_{2n}$, are only sparsely represented amongst the derivatives from natural products.

Acrolein (acrylic aldehyde), $C_2H_3 . COH$, yields on hydrogenation *allylic alcohol*, $C_2H_3 . CH_2 . OH$ (also obtainable in various other ways), existing as a thiocyanic ester in the oils of black mustard seed, horse radish, and garlic. Higher homologues of allylic alcohol are probably contained among the alcohols of the previous series obtained on saponifying sperm oil, since in certain cases a deficiency of hydrogen is observed on analysis, coupled with a strongly marked tendency

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[1] C. Hell (*Annalen*, ccxxiii., 269) based a method for the quantitative determination of higher alcohols on this reaction, the substance to be examined being heated to 300°-310° C. in contact with soda lime, and the evolved hydrogen collected and measured. At higher temperatures there is a possibility of hydrogen being also evolved by the action of caustic alkalis on oleic acid. This method has been found useful in the examination of beeswax (*q.v.*), which, when genuine, furnishes about 54 per cent. of myricylic alcohol.

to combine directly with iodine, indicating the presence of unsaturated compounds. These higher alcohols, however, have not as yet been isolated from the other bodies accompanying them in a state of sufficient purity to admit of their formulæ being exactly determined.

Borneol, $C_{10}H_{19} . OH$, occurs in the camphor of *Dryobalanops camphora*, and to a small extent in oil of valerian and oil of rosemary.

Alcohols of the series $C_n H_{2n-3} . OH$, derived from the $C_n H_{2n-2}$ (acetylene) series of hydrocarbons, are found to some extent in certain essential oils—*e.g.*, *geraniol*, $C_{10}H_{17} . OH$, in Indian geranium oil. This appears to be a true analogue of ethylic and allylic alcohols, being capable of yielding by oxidation an aldehyde and a monobasic acid (*geranic acid*), $C_9H_{15} . COH$ and $C_9H_{15} . COOH$ respectively. No substances of analogous character have as yet been isolated from fixed oils and fats, etc.

PHENOL AND ITS HOMOLOGUES.

Alcohols derived from hydrocarbons still poorer in hydrogen are occasionally met with as constituents of natural products of the resinous class, or as substances formed by destructive distillation. Thus the hydrocarbons of the benzene family, C_nH_{2n-6}, give rise to two classes such of alcohols, both indicated by the general formula $C_n H_{2n-7} . OH$ and derived from the same parent body, *phenol*, $C_6H_5 . OH$.

In the one class (*phenols proper*) the hydroxyl group is situated in connection with the "benzene nucleus" of 6 carbon atoms; and in the other (*benzylic alcohol series*) the hydroxyl group is not situated in the benzene radicle, but in one of the "side chains" introduced by the methylation of benzene so as to develop homologous hydrocarbons. Thus—

PHENOLS.	
Phenol (carbolic acid), ...	$C_6H_5 \ OH$
Cresol (methyl-phenol), ...	$C_6H_4\left\{\begin{matrix}CH_3\\OH\end{matrix}\right.$
Xylenol (dimethyl-phenol), . . .	$C_6H_3\left\{\begin{matrix}CH_3\\CH_3\\OH\end{matrix}\right.$
Phlorol (ethyl-phenol), ...	$C_6H_4\left\{\begin{matrix}C_2H_5\\OH\end{matrix}\right.$
BENZYLIC ALCOHOL SERIES.	
Benzylic alcohol, ...	$C_6H_5 . CH_2 . OH$
Xylylic alcohol, ...	$C_6H_4\left\{\begin{matrix}CH_3\\CH_2 . OH\end{matrix}\right.$
Benzyl-carbinol, ...	$C_6H_5 . CH_2 . CH_2 . OH$

Alcohols of the phenol class are, for the most part, contained in the tars derived from the destructive distillation of coal, wood, etc. *Benzylic alcohol* is contained as such in the volatile oil of cherry laurel, and in the form of a compound ester in balsam of Peru and liquid storax. A higher homologue, *sycocerylic alcohol*, $C_{18}H_{29} . OH$, is found as an acetic compound ester in the resin of *Ficus rubiginosa*, whilst *α-lactucerol* and *β-lactucerol*, two isomerides thereof, are contained as acetic esters in lettuce juice. *Quebrachol* (from quebracho bark), and *cupreol* and *cinchol* (from cinchona barks) are analogous substances isomeric with one another and indicated by the higher homologous formula $C_{20}H_{33} . OH$; whilst *Phasol* (from *Phaseolus vulgaris*) is a lower homologue, $C_{15}H_{23} . OH$.

All these substances are closely akin to *cholesterol*, *isocholesterol*, *phytosterol*, and *paraphytosterol*, alcoholiform substances belonging to the family derived from the hydrocarbons, $C_n H_{2n-8}$, and occurring in various fixed oils as normal constituents dissolved in the glycerides, etc., constituting the bulk of the oils.

It is extremely probable that other analogous substances are also contained in oils, etc. In the husks of *Phaseolus vulgaris* both paraphytosterol and phasol are present; when such substances occur in the vicinity of oil-containing tissues, obviously any process applicable for the extraction of the oil is extremely likely to dissolve out more or less of the accompanying alcoholiform substances, as well as any other substances soluble in oil that may happen to be contained in the seeds, etc., operated upon.

CHOLESTEROL SERIES AND ANALOGUES.

Cholesterol and its isomerides appear to be homologues of *cinnamic alcohol*, $C_9H_9 . OH$ (contained in storax as cinnamic ester), indicated by the formula $C_{26}H_{43} . OH$. Some (cholesterol—long known as a bile constituent—and isocholesterol) chiefly occur in oils, etc., of animal origin, such as whale and fish oils and wool-grease; others (phytosterol and isophytosterol) are found in vegetable oils, such as olive oil. *Ambergris* and *castoreum* (from the Castor beaver) also appear to contain related substances (*ambreol* and *castorol* respectively).

All these bodies, like the sycocerylic alcohol and its homologues above mentioned, are of alcoholiform character readily yielding acetic and benzoic compound esters (often of highly crystalline character, and readily purified in consequence), the melting points of which are characteristic. Thus, cholesterol heated with benzoic anhydride (preferably in a sealed tube at 200° C.) forms a compound ester almost insoluble in boiling alcohol, but crystallisable from ether in rectangular tables, melting at 150°-151° C.

The following table illustrates some of the differences between cholesterol and its isomerides:—

	Melting Point.	Action on Polarised Light.	Melting Point of Benzoic Ester.
	° C.		° C.
Cholesterol, . .	147	Lævo-rotatory	150-151
Isocholesterol, . .	137-138	Dextro-rotatory	190-191
Phytosterol, . .	132-133	Lævo-rotatory	. .
Paraphytosterol, .	149-150	Dextro-rotatory	. .

When dissolved in chloroform and treated with an equal volume of sulphuric acid, cholesterol yields a blood-red coloration, soon becoming cherry-red and purplish, permanent for several days; the acid underlying the chloroform solution exhibits a strong green fluorescence.

Phytosterol gives a similar coloration, becoming bluish-red on standing some days: whilst isocholesterol gives no colour at all. On treatment with acetic anhydride, compound esters are produced in each case, the "acetyl number" of which is 135·5 (parts of potassium hydroxide, KOH, neutralised by the acetic acid developed by the saponification of 1,000 parts of compound ester, Chap. VIII.); the corresponding values for the similar compound esters obtained from cetylic, cerylic, and myricylic alcohols being respectively 197·5, 128·1, and 116·7.

Another substance closely akin to phytosterol has been isolated from the seeds of *Lupinus luteus*—*i.e.*, *lupeol*[1]—probably indicated by the formula $C_{26}H_{32}O$, containing less hydrogen than phytosterol; this melts at 204°, is dextro-rotatory, and forms benzoic and acetic esters melting respectively at 250° and 230°; dissolved in chloroform and treated with acetic anhydride and sulphuric acid, it gives a reddish coloration, becoming intensely violet-red on standing. Several other substances of analogous character appear to be contained in various vegetable products—*e.g.*, *hydrocarotin* (carrots), *paracholesterol* (*Æthalium septicum*), etc., etc.; but their occurrence in oil-bearing seeds, and the oils obtained from them, has not yet been substantiated.

GLYCOLS.

It was shown by *Stürke*[2] that when carnauba wax is saponified, and the alcoholiform constituents thus set free fractionated by means of petroleum, glycol is obtained melting at 103·5 to 103·8, and giving numbers on analysis agreeing with the formula $C_{25}H_{52}O_2$, or $C_{23}H_{46}\left\{\begin{matrix} CH_2 \,.\, OH \\ CH_2 \,.\, OH \end{matrix}\right.$. This product evolves eight hydrogen atoms on fusion with caustic alkalis, forming an acid of the oxalic series, thus—

$$C_{23}H_{46}\left\{\begin{matrix} CH_2 \,.\, OH \\ CH_2 \,.\, OH \end{matrix}\right. + 2NaOH = 4H_2 + C_{23}H_{46}\left\{\begin{matrix} CO \,.\, ONa \\ CO \,.\, ONa \end{matrix}\right.$$

just as

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[1] Likiernik, *Ber.*, 1891, xxiv., 183 and 187.

[2] *Annalen*, ccxxiii., 283; also in abstract, *J. Soc. Chem. Ind.*, 1884, iii., 448.

cerylic alcohol and similar bodies evolve four hydrogen atoms forming an acid of the stearic series, thus—

$$C_{26}H_{53} . CH_2 . OH + NaOH = 2H_2 + C_{26}H_{53} . CO . ONa.$$

Hydrocarbons in Fish Oils.—Many fish liver-oils contain a large proportion of a hydrocarbon or hydrocarbons, which are separated with the unsaponifiable matter.

Tsujimoto[1] found that this hydrocarbon, to which he gave the name of *squalene*, was present in the oils from the livers of various species of Japanese sharks.

Chapman[2] isolated the same or a similar hydrocarbon from the oils derived from two species of Portuguese sharks. It formed the main constituent of the oil which it caused to give abnormal analytical values. This compound, to which *Chapman* gave the name of *spinacene*, is an unsaturated hydrocarbon having the formula $C_{30}H_{50}$. It contains six ethenoid linkages, and yields a dodecabromide, $C_{30}H_{50}Br_{12}$. It is optically inactive, does not solidify at — 20° C., and has specific gravity 0·8641 at 15°/15° C. When exposed to the air it absorbs oxygen rapidly and forms a hard film resembling linoxyn.

Oil from the liver of the basking shark was found by *Tsujimoto*[3] to contain, not only an unsaturated hydrocarbon, $C_{30}H_{50}$, but also a liquid saturated hydrocarbon, $C_{18}H_{33}$.

[1] *J. Ind. Eng. Chem.*, 1916, viii., 289.

[2] *J. Chem. Soc.*, 1917, cxi., 56; *Analyst*, 1917, xlii., 161.

[3] *J. Ind. Eng. Chem.*, 1919, ix., 1098.

CHAPTER III.

SAPONIFICATION PRODUCTS OF OILS, FATS, WAXES, ETC.

FATTY ACIDS.

It is a remarkable fact that all known compound esters contained in natural fixed oils and fats, etc., invariably give rise on saponification to *monobasic* acids only, dibasic acids (like oxalic acid), and acids of still higher basicity being conspicuous by their absence from the products thus formed, although in many cases readily obtainable from these products by simple operations in the laboratory.

At least six different groups of monobasic acids are represented amongst the saponification products of fixed oils, etc., four of which are included in the general formula $C_mH_{2n+1} . CO . OH$; according as $m = n$, or $= n + 1$, $n + 2$, or $n + 3$, this general formula represents the following groups :—

Formula of Acid.	Family.
$C_mH_{2m+1} . CO . OH$	Acetic (or stearic) series.
$C_mH_{2m-1} . CO . OH$	Acrylic (or oleic) series.
$C_mH_{2m-3} . CO . OH$	Propiolic (or linolic) series.
$C_mH_{2m-5} . CO . OH$	Linolenic series.
$C_mH_{2m-7} . CO . OH$	Clupanodonic series.

Two other groups are more highly oxidised, being included in the general formula $C_mH_{2n}\left\{\begin{matrix}OH\\CO . OH\end{matrix}\right.$; according as $m = n$ or $= n + 1$ the following two groups result :—

Formula of Acid.	Group.
$C_mH_{2m}\left\{\begin{matrix}OH.\\CO . OH.\end{matrix}\right.$	Hydroxyacetic (hydroxystearic or glycolic) series.
$C_mH_{2m-2}\left\{\begin{matrix}OH.\\CO . OH.\end{matrix}\right.$	Hydroxyacrylic (hydroxyoleic or ricinoleic) series.

In addition to these six leading groups of monobasic acids, representatives of several others can be obtained by saponification from various essential oils and allied products; whilst by gentle oxidation processes or other reactions several different kinds of more oxidised monobasic acids are readily formed from the normal "fatty acids" derived from natural fixed oils, etc. Thus, for example :—

Formula of Acid.	Group.	Examples and Sources.
$C_mH_{2m-7} . CO . OH$	Benzoic series	Benzoic and toluic acids, &c.; from gum benzoin, balsam of Tolu, dragon's blood, storax, oil of bitter almonds, &c.
$C_mH_{2m-9} . CO . OH$	Cinnamic series	Cinnamic acid; from oil of cinnamon, cassia, storax, balsam of Tolu, &c
$C_mH_{2m-8} \left\{ \begin{matrix} OH \\ CO . OH \end{matrix} \right.$	Hydroxybenzoic (salicylic) series	Salicylic acid; from gaultheria oil, &c.
$C_mH_{2m-1} \left\{ \begin{matrix} OH \\ OH \\ CO . OH \end{matrix} \right.$	Glyceric (dihydroxystearic) series	Oxidation of oleic acid and its isomerides and homologues.
$C_mH_{2m-2} \left\{ \begin{matrix} (OH)_3 \\ CO . OH \end{matrix} \right.$	Erythroglucic (trihydroxystearic) series	$C_{18}H_{36}O_5$; from oxidation of ricinoleic acid and its isomerides.
$C_mH_{2m-3} \left\{ \begin{matrix} (OH)_4 \\ CO . OH \end{matrix} \right.$	Tetrahydroxystearic series	$C_{18}H_{36}O_6$ (sativic acid); from oxidation of linolic acid.
$C_mH_{2m-5} \left\{ \begin{matrix} (OH)_6 \\ CO . OH \end{matrix} \right.$	Hexahydroxystearic series	$C_{18}H_{36}O_8$ (linusic acid); from oxidation of linolenic acid.

ACETIC GROUP OF FATTY ACIDS.

The table on pp. 23 and 24 shows the leading acids of the acetic group (general formula $C_nH_{2n}O_2 = C_mH_{2m+1} . CO . OH$) derived from fixed oils, waxes, essential oils, and similar sources. In addition numerous isomeric modifications of many of the acids are known, which have been obtained artificially by synthetic and other laboratory operations.

The formulæ ascribed to several of the acids named in the following table can hardly be regarded as established with perfect certainty. Thus the *cocinic acid*, $C_{11}H_{22}O_2$, formerly supposed to be contained in coconut oil, appears from later researches to be in all probability only a mixture of other acids of the series; and the same remark applies to the *tridecoic acid*, $C_{13}H_{26}O_2$, from the same source, which appears to be simply a mixture of lauric and myristic acids.

Similarly, *cetic acid*, $C_{15}H_{30}O_2$, and the isomeric (?) *benomargaric* and *stillistearic* acids are very doubtful bodies; the last has been stated by later observers to be simply palmitic acid, and benomargaric acid to be a mixture of palmitic and myristic acids.

The *margaric acid*, $C_{17}H_{34}O_2$, formerly regarded as present in animal fats, has been since shown to consist, at all events in many cases, of a mixture of stearic and palmitic acids and more or less oleic acid.[1] Again, the compositions ascribed to *medullic acid*, $C_{21}H_{42}O_2$; *hyænic acid*, $C_{25}H_{50}O_2$; *geoceric acid*, $C_{26}H_{52}O_2$; and *theobromic acid*,

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[1] The margarine or oleomargarine used as a butter substitute is essentially a mixture of the glycerides of stearic and palmitic acids with sufficient olein to give it its soft texture.

Formula.	Name of Acid.	Boiling Point.	Melting Point.	Sources.
CH_2O_2	Formic,	101° C.	8° C.	Ants ; nettles.
$C_2H_4O_2$	Acetic,	118°	17°	Acetic fermentation ; oil of cow parsnep, and various other essential oils.
$C_3H_6O_2$	Propionic or Tritylic,	140°	..	Oxidation of propylic alcohol from fermented fusel oil.
$C_4H_8O_2$	Normal Butyric,	162°	−6·5°	Cow's butter ; perspiration ; oil of cow parsnep
	Isobutyric,	153°	..	Oxidation of isobutylic alcohol from fusel oil ; Roman chamomile oil.
$C_5H_{10}O_2$	Isovaleric,	173·7°	−51°	Several isomerides known. Valerian root ; Isovaleric acid from fat of *Delphinus phocæna*.
$C_6H_{12}O_2$	Caproic or Hexoic,	200°	−8°	Isohexoic acid (isobutyl-acetic acid) from cow's butter and coconut oil.
		205°	−1·5°	Normal hexoic acid, as octylic ester in oil of *Heracleum*.
$C_7H_{14}O_2$	Œnanthic or Heptoic,	222°	−10·5°	Normal acid by oxidation of œnanthol from castor oil ; wine fusel oil.
$C_8H_{16}O_2$	Caprylic or Octoic,	238°	16·5°	Isoprimary acid from coconut oil and butter ; Limburg cheese.
$C_9H_{18}O_2$	Pelargonic or Ennoic,	254°	13°	Normal acid from oil of *Pelargonium roseum ;* and oxidation of oil of rue and beetroot fusel oil.
$C_{10}H_{20}O_2$	Capric or Decoic,	269°	31·3°	Butter ; coconut oil ; grape fusel oil.
$C_{11}H_{22}O_2$	Hendecoic or Undecylic,	228° at 160 millims. pressure.	28·5°	Hydrogenation of Hendecenoic acid from distillation of castor oil.
$C_{12}H_{24}O_2$	Lauric or Dodecoic,	225° at 100 millims. pressure.	43·5°	Laurel butter (*Laurus nobilis*) ; Pichurim bean fat ; coconut oil ; palm-kernel oil.
$C_{13}H_{26}O_2$	Tridecoic,	..	..	Supposed to be contained in coconut oil ; doubtful.
$C_{14}H_{28}O_2$	Myristic,	250° at 100 millims. pressure.	53·8°	Nutmeg butter ; coconut oil ; dika fat ; croton oil ; spermaceti.
$C_{15}H_{30}O_2$	Pentadecoic,	..	55°	(?) Oil of *Jatropha curcas*.
		..	53·5°	Cetic acid (?) from spermaceti.

Formula.	Name of Acid.	Boiling Point.	Melting Point.	Sources.
$C_{15}H_{30}O_2$	Pentadecoic,	..	53°	Benomargic acid (?) from oil of Ben. Stillistearic acid (?) from *Stillingia sebifera.*
$C_{16}H_{32}O_2$	Palmitic,	271·5° at 100 millims. pressure.	62·6°	Palm oil. One of the constituents of most animal fats. Spermaceti; beeswax; Japan wax.
$C_{17}H_{34}O_2$	Margaric,	..	60°	From cetyl cyanide; possibly in certain fats.
	Daturic,	..	55°	From oil of *Datura stramonium;* doubtful.
$C_{18}H_{36}O_2$	Stearic,	291°at 100 millims. pressure.	69·3°	Tallow, lard, and most animal solid fats; Shea butter; Illipé fat.
$C_{19}H_{38}O_2$	Enneadecoic,	..	66°	From stearyl cyanide (?) obtained along with artificial margaric acid.
$C_{20}H_{40}O_2$	Arachic (or Arachidic); Butic,	..	77°	Earth-nut oil (*Arachis hypogæa*); butter (?) (*Heintz*); rape-seed oil; mustard-seed oil.
$C_{21}H_{42}O_2$	.. ..	..	72·5°	Medullic acid (?) from beef marrow.
$C_{22}H_{44}O_2$	Benic or Behenic,	..	80°-82°	Oil of Ben; black mustard-seed oil; rape oil.
$C_{22}H_{46}O_2$	.. ..	..	..	.. ..
$C_{24}H_{48}O_2$	Lignoceric,	..	80·5°	Earth-nut oil; beechwood tar.
	Carnaubic,	..	72·5°	Carnauba wax.
$C_{25}H_{50}O_2$	Hyænic,	..	78°	Hyæna fat; doubtful.
$C_{26}H_{52}O_2$	.. ..	..	..	Geoceric acid (?) from distillation of brown coal.
$C_{27}H_{54}O_2$	Cerotic,	..	78°	Beeswax; Carnauba wax; Chinese wax.
$C_{28}H_{56}O_2$	.. ..	..	..	.. ..
$C_{29}H_{58}O_2$	.. ..	..	..	.. ..
$C_{30}H_{60}O_2$	Melissic,	..	88·5°	Oxidation of myricylic alcohol from beeswax.
$C_{31}H_{62}O_2$	.. ..	..	..	.. ..
$C_{64}H_{128}O_2$	Theobromic,	..	72°	Cacao butter.

$C_{64}H_{128}O_2$,[1] require confirmation as regards the individual character and purity of these substances.

Of those acids where the carbon present lies between C_{10} and C_{27}, it is noticeable that those of most frequent and widely-spread occurrence, and of which the compositions are known with certainty, always

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[1] Graf was unable to find any theobromic acid in cacao butter (*Arch. Pharm.*, 1888, xxvi., 830).

contain an *even* number of carbon atoms. Hence it has been supposed by some chemists that acids containing an *odd* number of carbon atoms do not actually occur as glycerides amongst the natural oils and fats, and that the bodies supposed to possess such a composition are really either mixtures of glycerides with even numbers of carbon atoms, or substances rendered otherwise impure. *A priori*, however, there seems no reason for doubting the possibility of the existence in nature of glycerides of acids containing an odd number of carbon atoms, and mixed glycerides containing the so-called margaric acid have been described. The fatty acids obtained from a mixed glyceride of olive oil by *Holde* and *Stange*[1] melted at 53°-55° C. By fractionation with magnesium acetate it was not found possible to precipitate a substance melting above 61° C., although artificial mixtures of palmitic acid and stearic acid melting at 55° C. could be readily separated into their constituents. Hence, this fact, in conjunction with the iodine and saponification values, was regarded as a proof that the acid was a definite compound of the formula $C_{17}H_{34}O_2$ (*margaric acid*).

Nördlinger[2] also claimed to have isolated about 1 per cent. of *daturic acid* from palm oil, but his statement has not been confirmed.

In a later communication *Holde*[3] shows that it is not safe to regard a fatty acid as a chemical individual, even when four or five successive fractions are nearly constant in melting point. For example, the "heptadecylic" acid, $C_{17}H_{34}O_2$, which *Kreis* and *Hafner* separated from olive oil, after a very large number of fractionations, yielded stearic acid (melting point 68° to 69° C.). In like manner Gérard's "daturic" acid, when fractionated in large quantities, yielded a fatty acid with a molecular equivalent of 329 and melting points of 57° to 58·5° C. to 63°-64° C.

The substance prepared by *Nördlinger*[4] from palm oil was examined in a similar way. Several successive fractions showed an apparently constant melting point of 56° C. and the molecular equivalent of heptadecylic acid, but, finally, after repeated crystallisation, an acid melting at 68° to 68·5° C. and with a molecular equivalent of 288 was isolated. The apparent constancy of the earlier fractions was attributed to there being present an intimate admixture of palmitic acid with fatty acids of very high molecular weight. Subjected to this treatment, the "margaric" acid separated by *Holde* and *Stange* (*supra*) was also found to be a mixture.

In the case of butter fat, coconut oil, and some few other substances, fatty acids of low molecular weight (*i.e.*, where n in the general formula $C_nH_{2n}O_2$ is of low value), are present to some notable extent; but, as a general rule, natural oils and fats rarely yield fatty acids of this description where n has a smaller value than 12. Inasmuch as the lower members of the acetic acid family are comparatively easily volatile (especially with water vapour), whilst the higher ones are almost non-volatile with ordinary steam, this practically means

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[1] *Ber.*, 1900, xxxiv., 2402.

[2] *Ibid.*, 1892, xxv., 578.

[3] *Ber.*, 1905, xxxviii., 1247.

[4] *Zeit. angew. Chem.*, 1892, 110.

that the fatty acids from most fats and oils *will not readily distil by the aid of moist steam*, whilst a certain proportion of more easily volatile acids is contained in the mixture of acids obtained from butter fat and coconut oil, etc. This distinction is utilised in certain cases as a means of testing the quality of such substances as regards adulteration and admixture with cheaper forms of fatty matter (Reichert's test, *vide* Chap. VIII.).

The fatty acids of the acetic series differ considerably in their respective degrees of solubility in water. The lowest members—formic, acetic, propionic, and butyric acids—are miscible with water in all proportions; the highest members, including myristic acid and all above it, are quite insoluble in water; the intermediate acids exhibit a degree of solubility which is the greater the lower the molecular weight. Thus caprylic acid dissolves in 400 parts of boiling water, and capric acid in about 1,000 parts, both largely separating out again on cooling; whilst lauric acid is almost insoluble in cold water, though sparingly dissolved by boiling water.

Alcohol, especially when warm, readily dissolves even the highest members of the series. Since the glycerides of these acids are, as a rule, almost insoluble in alcohol, this property affords a method of separating the free fatty acids contained in natural oils, etc., from the glycerides, the oil being simply agitated with alcohol and allowed to stand so as to separate the alcoholic solution of fatty acids from the unaffected glycerides. Alcohol containing only a minute quantity of a free fatty acid exhibits an acid reaction to phenol-phthalein, and can therefore be readily titrated by means of a weak standard alkaline solution in presence of that indicator. On this also is based the general method of determining the amount of fatty acid salt formed on saponifying a glyceride or other compound ester by an alkali (Chap. VIII.). The highest acids of the series are not extremely soluble in cold alcohol, so that they are readily crystallisable from that liquid.

The normal salts of acids of the acetic family are indicated by the general formula $C_nH_{2n+1} . CO . OM$, where M is a monad metal. Acid salts of formula $C_nH_{2n-1}O_2M, C_nH_{2n}O_2$ can in some cases be produced —*e.g.*, sodium diacetate, $C_2H_3NaO_2, C_2H_4O_2$; potassium distearate, $C_{18}H_{35}KO_2, C_{18}H_{36}O_2$. Salts of this kind when dissolved in hot alcohol show an acid reaction with phenol-phthalein, and behave toward alkaline solutions on titration in presence of that indicator precisely as mixtures of the free acid and the neutral salt.

In certain cases the neutral alkali salts are partly hydrolysed by solution in water with formation of an acid salt and caustic alkali. Thus, in the case of neutral sodium stearate, we have—

$$\overset{\text{Neutral Sodium Stearate.}}{2C_{18}H_{35}NaO_2} + \overset{\text{Water.}}{H_2O} = \overset{\text{Sodium Hydroxide.}}{NaOH} + \overset{\text{Sodium Distearate.}}{C_{18}H_{35}NaO_2, C_{18}H_{36}O_2}$$

By adding common salt to the fluid, the latter compound and the unaltered neutral salt are thrown out of solution. On dissolving the precipitate in alcohol and titrating the solution an amount of acidity is registered precisely equivalent to the alkalinity of the aqueous fluid. On the occurrence of this phenomenon depends a good deal of the cleansing properties of soaps, the action being also noticeable in the case of the alkali salts of oleic and ricinoleic acids to approximately the same extent as with those of palmitic and stearic acids (Chap. XXII.).

ACRYLIC (OLEIC) GROUP OF FATTY ACIDS.

The total number of acids of general formula $C_nH_{2n-1} . CO . OH$ now known is somewhat considerable. As in the case of the acetic group, only a comparatively small number of them are contained in natural fats, etc., and of these but few are of relatively low molecular weight so as to be readily volatile. The table on p. 28 exhibits the more important acids of this class.

As also in the case of the acetic group of acids, the existence of certain members mentioned in the table is not yet established with perfect certainty. Thus *damaluric acid* is a substance the existence of which requires confirmation. The existence of hypogæic acid has been defined by *Schön*, who found the only acid of the acrylic series present in arachis oil to be oleic acid, but, on the other hand, it has been found in maize oil (*q.v.*). Similarly, moringic acid has been stated by more recent observers to be simply impure oleic acid; and according to *Schädler*, the same remark applies to doeglic acid, this being regarded by him as simply impure physetoleic acid.

The unsaturated nature of the hydrocarbons from which this group of fatty acids are derived leads to their possession of some peculiar features. Thus, when heated with fused alkali (potassium hydroxide), there is a tendency to undergo a change indicated by the general equation—

$$C_{m+n}H_{2(m+n-1)}O_2 + 2KOH = K . C_mH_{2m-1}O_2 + K . C_nH_{2n-1}O_2 + H_2$$

the potassium salts of *two acids of the acetic group* being formed together with free hydrogen. In virtue of this tendency, oleic acid, when thus treated, forms palmitic and acetic acids, a circumstance on which a manufacturing process was formerly based.

$$\begin{array}{ccccccccc} \text{Oleic Acid.} & & \text{Potassium Hydroxide.} & & \text{Potassium Palmitate.} & & \text{Potassium Acetate.} & & \\ C_{18}H_{34}O_2 & + & 2KOH & = & K . C_{16}H_{31}O_2 & + & K . C_2H_3O_2 & + & H_2. \end{array}$$

Absorption of Halogens.—Again, inasmuch as the unsaturated hydrocarbons have a more or less marked tendency to combine directly with halogens (and so pass into the series of substitution derivatives of the saturated hydrocarbons), the same tendency is shared by the fatty acids derived from them; thus the hydrocarbon ethylene, as has long been known, combines directly with chlorine forming an oily fluid,[1] originally known as "Dutch liquid," the reaction being—

$$\begin{array}{ccccc} \text{Ethylene.} & & \text{Chlorine.} & & \text{Ethylene Dichloride.} \\ H_2C = CH_2 & + & Cl_2 & = & H_2ClC - CClH_2 \end{array}$$

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[1] Whence the odd name *olefiant gas* for ethylene, signifying "oil making" gas.

Formula.	Name of Acid.	Boiling Point.	Melting Point.	Sources.
$C_3H_4O_2$	Acrylic,	140° C.	8° C.	Oxidation of acroleïn from glycerol.
$C_4H_6O_2$	Crotonic,	185°	72°	From cyanide of allyl (derived from oil of mustard).
$C_5H_8O_2$	Angelic,	185°	45°	Angelica root. Sumbul root resin.
	Tiglic,	196°	64°	Oil of chamomile. Croton oil.
$C_6H_{10}O_2$	Pyroterebic,	210°	...	Action of heat on terebic acid from oil of turpentine and nitric acid.
$C_7H_{12}O_2$	... ...	...	53°	Damaluric acid (?) (from cow's and horse's urine).
$C_8H_{14}O_2$	Octenoic,	...	...	... ...
$C_9H_{16}O_2$	Ennenoic,	...	liquid.	Œnanthol (from castor oil) and acetic anhydride.
	Phoronic,	...	169°	Oxidation of sodium camphor.
$C_{10}H_{18}O_2$	Decenoic,	242°-269°	10°-86°	Several isomeric modifications known ; all of artificial origin.
$C_{11}H_{20}O_2$	Hendecenoic,	275°	24·5°	Castor oil distilled under diminished pressure.
	Petroleumic,	250°-260°	...	Contained in petroleum.
$C_{12}H_{22}O_2$	Dodecenoic,	...	liquid.	Artificial.
$C_{13}H_{24}O_2$	Tridecenoic,	...	...	... ...
$C_{14}H_{26}O_2$	Tetradecenoic,	...	...	... ...
$C_{15}H_{28}O_2$	Moringic,	...	0°	Oil of ben.
	Cimicic,	...	44°	Fœtid oil from *Raphigaster punctipennis*.
$C_{16}H_{30}O_2$	Physetoleic,	...	30°	Sperm oil.
	Hypogæic,	...	34°	Earthnut oil (*Arachis hypogæa*). Maize oil.
			50°	Aldepalmitic acid (?) from butter.
$C_{17}H_{32}O_2$	Heptadecenoic,	...	...	... ...
$C_{18}H_{34}O_2$	Oleic,	286° at 100 millims. pressure.	14°	Contained as glyceride in most animal fats and many vegetable oils.
	Isoleic,	...	44°-45°	Distillation of hydroxystearic acid.
	Stearidic,	...	35°	Action of water on silver bromostearate.
	Rapic,	...	...	As a glyceride in rape oil.
$C_{19}H_{36}O_2$	Doeglic,	...	A little above 0°.	Oil from dœgling (bottlenose whale).
$C_{20}H_{38}O_2$	... ...	...	...	... ...
$C_{21}H_{40}O_2$	... ...	...	...	... ...
$C_{22}H_{42}O_2$	Erucic,	254-·5° at 10 millims. pressure.	34°	Colza, grape seed, mustard, and marine animal oils.

In a similar way, oleic acid and its congeners, being derivatives of ethylene of general formula $R.\mathrm{CH}=\mathrm{CH}.S$, will directly combine with bromine or iodine in parallel fashion, forming dibromo-, or di-iodosubstitution derivatives of acids of the acetic family of form $R . CHBr - CHBr . S$; thus—

$$\overset{\text{Oleic Acid.}}{C_{18}H_{34}O_2} + \overset{\text{Iodine.}}{I_2} = \overset{\text{Di-iodostearic Acid.}}{C_{18}H_{34}I_2O_2}$$

This reaction is utilised as a convenient method of distinguishing from one another acids derived respectively from saturated hydrocarbons, and from unsaturated hydrocarbons of the olefine series, the former not combining with halogens, and the latter uniting with them in the proportion of one molecule of fatty acid to two atoms of halogen. Accordingly, the measurement of the quantity of iodine or bromine thus fixed ("iodine value," or "bromine value") often gives useful information as to the nature of the fatty acid or acids present; and the same remark applies equally to the glycerides themselves, which also combine with halogens in the like manner, *e.g.* :—

$$\overset{\substack{\text{Olein, Glyceride of} \\ \text{Oleic Acid.}}}{C_3H_5(C_{18}H_{33}O_2)_3} + \overset{\text{Iodine.}}{3I_2} = \overset{\substack{\text{Glyceride of Di-iodo-} \\ \text{stearic Acid.}}}{C_3H_5(C_{18}H_{33}I_2O_2)_3}$$

Oleic Acid.—This fatty acid is of very common occurrence, forming a principal constituent of the liquid portion of most fats and oils. At the ordinary temperature it is a colourless liquid, which, on exposure to the air, rapidly absorbs oxygen, becoming more or less yellowish-brown. It melts at 14° C. and solidifies at 4° C. Its specific gravity is 0·898 at 14° C. and 0·900 at 15° C. Under a reduced pressure (10 mm.) it boils at 223° C., but undergoes decomposition when heated at the ordinary pressure, although it can be distilled unchanged in a current of superheated steam (250° C.) or superheated alcohol.

Lewkowitsch,[1] mainly from a consideration of the products formed on treating oleic acid with sulphuric acid, concluded that the following formulæ were the most probable for oleic and iso-oleic acids :—

$$C_{13}H_{25} - CH_2 - \overset{\gamma}{C}H = \overset{\beta}{C}H - CH_2 - CH_2 - COOH$$

Oleic Acid.

$$C_{13}H_{25} - CH_2 - CH_2 - \overset{\beta}{C}H = \overset{\alpha}{C}H - COOH$$

Iso-oleic Acid.

This constitutional formula for oleic acid is very different from that suggested by *Baruch*,[2] viz. :—

$$C_8H_{17} - CH = CH - (CH_2)_7 - COOH$$

Absorption of Hydrogen.—In just the same kind of way certain acids of the acrylic family can combine directly with nascent hydrogen produced under appropriate conditions, becoming thereby converted

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[1] *J. Soc. Chem. Ind.*, 1897, xvi., 391.

[2] *Ber.*, 1894, xxvii., 173.

into acids of the acetic group, the general reaction expressing the change being—

$$C_nH_{2n-2}O_2 \quad + \quad H_2 \quad = \quad C_nH_{2n}O_2$$

Thus, oleic acid forms stearic acid when heated in a sealed tube with fuming hydriodic acid and phosphorus. By reversing the process, an acetic acid becomes transformed into an acrylic acid. In practice, the direct removal of hydrogen after this fashion is difficult to accomplish; but in certain cases it may be effected by acting on the acid of the acetic group with chlorine or iodine or bromine, so as to produce a monochloro-, iodo-, or bromo-substitution derivative. By treating this with alkalis, etc., the elements of HCl, HI, or HBr are eliminated, leaving an acid of the acrylic series.

In this way acrylic acid itself is formed from iodopropionic acid; thus—

$$\begin{array}{ccccc} \text{Iodopropionic Acid.} & & & & \text{Acrylic Acid.} \\ C_3H_5IO_2 & - & HI & = & C_3H_4O_2 \end{array}$$

the elimination of the elements of hydriodic acid being brought about by treatment with sodium ethylate, lead oxide, or similar basic substances.

In other cases a dibromo- or dichloro-substitution derivative of an acid of the acetic family is acted upon with zinc dust, or other substance having a strong tendency to combine with halogens. Thus dibromopropionic acid and zinc dust form acrylic acid.

$$\begin{array}{ccccc} \text{Dibromopropionic Acid.} & & & & \text{Acrylic Acid.} \\ C_3H_4Br_2O_2 & - & Br_2 & = & C_3H_4O_2 \end{array}$$

In this way the dibrominated and di-iodised products obtained by adding Br_2 or I_2 to the higher acrylic acids can be made to reproduce the original acid. This reaction is utilised in the examination of oils, etc., containing the glycerides of unsaturated acids. Bromine addition products are formed and separated from one another by crystallisation, etc., and then debrominated so as to reproduce the original acids, which can thus be indirectly separated from one another in a fashion usually impracticable with the actual acids themselves.

Direct addition of hydrogen in presence of a catalytic agent such as palladium or nickel is among the most important developments of recent years in the oil industry (see *Hydrogenation of Oils*).

Addition of Sulphuric Acid.—Acrylic acids, at any rate in certain cases, combine directly with sulphuric acid, forming saturated compound sulphuric acids analogous to ethylsulphuric acid (sulphovinic acid); thus—

$$\begin{array}{ccccc} \text{Oleic Acid.} & & \text{Sulphuric Acid.} & & \text{Hydroxystearosulphuric Acid.} \\ C_{17}H_{33}\,.\,CO\,.\,OH & + & SO_2(OH)_2 & = & C_{17}H_{34}\left\{\begin{array}{l} O\,.\,SO_2\,.\,OH \\ CO\,.\,OH \end{array}\right. \end{array}$$

By the action of water, etc., on the compounds thus formed hydrolysis is brought about, with the formation of sulphuric acid and an acid of the hydroxyacetic (glycollic) group; thus—

$$\overset{\text{Hydroxystearosulphuric Acid.}}{C_{17}H_{34}\left\{\begin{array}{l}O \, . \, SO_2 \, . \, OH \\ CO \, . \, OH\end{array}\right.} + \overset{\text{Water.}}{H_2O} = \overset{\text{Sulphuric Acid.}}{SO_2(OH)_2} + \overset{\text{Hydroxystearic Acid.}}{C_{17}H_{34}\left\{\begin{array}{l}OH \\ CO \, . \, OH\end{array}\right.}$$

These reactions, especially the first, are utilised in the production of certain kinds of "Turkey red oils." Obviously the sum of the two changes is equivalent to the addition to an acrylic acid of the elements of water.

Formation of Hydroxy Acids.—The dibromides of acids of the oleic series, when treated with silver hydroxide, etc., form silver bromide together with glyceric acids—*i.e.*, di-hydroxy acids of the acetic series :—

$$C_nH_{2n-1}\left\{\begin{array}{l}Br_2 \\ CO \, . \, OH\end{array}\right. + 2AgOH = 2AgBr + C_nH_{2n-1}\left\{\begin{array}{l}(OH)_2 \\ CO \, . \, OH\end{array}\right.$$

By the regulated action of potassium hydroxide, they lose successively HBr and 2HBr, forming in the one case *bromoleic acid* or a homologue, and in the other case a propiolic acid—

$$C_nH_{2n-1}\left\{\begin{array}{l}Br_2 \\ CO \, . \, OH\end{array}\right. - HBr = C_nH_{2n-2}\left\{\begin{array}{l}Br \\ CO \, . \, OH\end{array}\right.$$

$$C_nH_{2n-1}\left\{\begin{array}{l}Br_2 \\ CO \, . \, OH\end{array}\right. - 2HBr = C_nH_{2n-3} \, . \, CO \, . \, OH$$

Elaidin Reaction.—A remarkable property possessed by many acids of the oleic group is that contact with certain reagents, more especially nitrous acid, converts them into isomeric modifications of higher fusing and boiling points, so that acids liquid at the ordinary temperature are converted into solids. This effect is also produced with the natural glycerides of these acids, forming a reaction largely utilised in testing the purity of certain oils (Chap. VII.). Oleic acid, liquid at ordinary temperatures, thus becomes *elaidic acid*, melting at 45° C., by contact with nitrous acid; and its glyceride, olein, fluid at 0° C., is similarly converted into *elaidin*, melting at 32° C.; whence the term "Elaidin reaction" applied to this nitrous acid test. In like manner erucic acid, melting at 34° C., is changed into *brassaidic* or *brassic*[1] *acid*, fusing at 60° C.; whilst parallel changes are undergone by hypogæic and physetoleic acids.

Elaidic acid and the other acids of this class which have undergone this change can be distilled unaltered under diminished pressure without being re-converted into the original acids; for a given pressure the boiling point is always slightly higher than that of the original acid. Thus *Krafft* and *Noerdlinger*[2] obtained the numbers.

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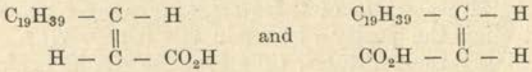
[1] The term "brassic acid" (*brassicasäure*) was originally applied to the acid, $C_{22}H_{42}O_2$, obtained from various species of *Brassica*, there being at that time some doubt whether "erucic acid" obtained from other analogous sources was or was not identical therewith. Later on the identity was established, and the term "brassäidic acid" (*brassidinsäure*) was applied to the product of nitrous acid on erucic acid to indicate its analogy with elaidic acid (Haussknecht, *Annalen der Chem. und Pharm.*, 1867, xcliii., 55).

[2] *Ber.*, 1889, xxii., 819.

Millimetres of Mercury.	Oleic Acid.	Elaidic Acid.
	° C.	° C.
100	285·5-286	287·5-288
50	264	266
30	249·5	251·5
15	232·5	234
10	223	225
	Erucic Acid.	Brassic Acid.
	° C.	° C.
30	281	282
15	264	265
10	254·5	256

From Erycic Acid.	Melts at	From Brassic Acid.	Melts at
Dihydroxybenic acid, .	132°-133° C.	Isodihydroxybenic acid, .	98°-99° C.
Dibromide of erucic acid,	42°-43° C.	Dibromide of brassic acid, .	54° C.
Dichloride, . . .	46° C.	Dichloride ,, ,, .	65° C.
Methylester from dichloride,	30·5° C.	Methylester from dichloride,	42·5° C.

According the the researches of *Holt* [1] the isomerism of erucic and brassic acids is of the *stereochemical* order—*i.e.*, the "structures" of the two bodies, when expressed in space of three dimensions, are not superposible; a difference only imperfectly expressible on a flat surface by the formulæ—



$$\begin{array}{ccc} C_{19}H_{39} - \overset{}{C} - H & & C_{19}H_{39} - C - H \\ \Vert & \text{and} & \Vert \\ H - C - CO_2H & & CO_2H - C - H \end{array}$$

The nature of the chemical change ensuing during the elaidin reaction is somewhat uncertain. By fusion with potassium hydroxide both oleic and elaidic acids yield acetate and palmitate; on the other hand, by oxidation with alkaline permanganate they form two different dihydroxystearic acids, melting repectively at 136·5° C. (solidifying at 119° C.) and 99°-100° C. (solidifying at 85°-86° C.—*Saytzeff*). Similarly erucic and brassic (brassäidic) acids give rise to two different dihydroxybenic acids on oxidation, as well as different derivatives of other kinds.

Chlorohydroxy Addition Compounds.—*Albitzky* [2] prepared these by treating an aqueous solution of the respective potassium salts with a solution of hypochlorous acid prepared by passing chlorine into a solution of sodium hydroxide cooled in ice. The excess of hypochlorous acid was removed by means of sulphurous acid, and the fatty acids liberated with sulphuric acid. The HClO addition compounds of oleic and erucic acid are thick oily liquids, whilst those of elaidic, brassic, and iso-erucic acids are semi-solid.

[1] *Ber.*, 1891, xxiv., 4120.

[2] *J. prakt. Chem.*, 1900, lxi., 65.

On heating chlorhydroxy-elaidic acid for six to seven hours in a sealed tube at 150°-160° C., a dihydroxystearic acid is obtained, identical with that formed by the oxidation of oleic acid with permanganate. Similarly chlorhydroxystearic acid from oleic acid yields the normal dihydroxystearic acid of elaidic acid, and the same phenomenon occurs in the case of the chlorhydroxybehenic acids from erucic acid and its isomer brassic acid.

Conversion of Elaidic Acid into Oleic Acid.—*Albitzky*[1] obtained, among other products, 12 grammes of oleic acid by heating 66 grammes of elaidic acid with 1½ volumes of a freshly-prepared saturated solution of sulphur dioxide in a sealed tube for seventeen hours at 200° C.

Chlorostearic Acid is obtained by *Albitzky*[2] by saturating a solution of elaidic acid in glacial acetic acid with hydrochloric acid gas, and heating the mixture in a glass tube at 150° C. The oily mass, which separates on the addition of water, is then recrystallised from alcohol until it melts at 38°-41° C. This substance exhibits the phenomenon of a double melting point; for when the crystals are again heated the melting point becomes 20°-21° C. On now being allowed to solidify again in a desiccator it is partially converted into a modification of higher melting point.

A chlorostearic acid, which has the same melting points and yields the same oxidation products, is obtained, though with more difficulty, from oleic acid.

Isomerides of Oleic Acid.—Besides elaidic acid (formed from oleic acid by contact with nitrous acid), two other acids isomeric with oleic acid are known—viz., *isoleic* and *stearidic* acids. There are also other isomerides of the anhydride character known.

Isoleic acid is obtained by acting on oleic acid with sulphuric acid, when combination takes place with the formation of *oxystearo-sulphuric* acid (probably two different modifications), thus—

$$C_{17}H_{33}\,.\,CO\,.\,OH + H_2SO_4 = C_{17}H_{34}\left\{\begin{matrix}O\,.\,SO_3H\\ CO\,.\,OH\end{matrix}\right.$$

By hydrolysis the product forms *hydroxystearic acid* (again, probably more than one modification), which on distillation under diminished pressure becomes dehydrated, furnishing a mixture of ordinary oleic acid and a solid isomeride, *isoleic acid*.

$$C_{17}H_{34}\left\{\begin{matrix}O\,.\,SO_3H\\ CO\,.\,OH\end{matrix}\right. + H_2O = H_2SO_4 + C_{17}H_{34}\left\{\begin{matrix}OH\\ CO\,.\,OH\end{matrix}\right.$$

$$C_{17}H_{34}\left\{\begin{matrix}OH\\ CO\,.\,OH\end{matrix}\right. = H_2O + C_{17}H_{33}\,.\,CO\,.\,OH$$

By converting the acids into zinc salts and heating the latter with alcohol a solution is obtained from which zinc isoleate separates on cooling, the other zinc salt remaining in solution. The acid obtained from the pure zinc salt by decomposition with a mineral acid, crystallises from ether; it melts at 45° C., but is not identical with elaidic acid which fuses at nearly the same temperature. Like oleic and

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[1] *J. prakt. Chem.*, 1900, lxi., 65.

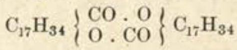
[2] *J. prakt. Chem.*, 1900, lxi., 94.

elaidic acids it forms acetate and palmitate on fusion with potassium hydroxide; but the dibromide formed by combination with bromine when treated with silver hydroxide yields a dihydroxystearic acid melting at 77°-78° C. and solidifying at 65°-66° C., the same substance being also formed by oxidising isoleic acid with alkaline permanganate. On the other hand, the dihydroxystearic acids obtained by oxidising oleic and elaidic acids in the same way melt at 136·5° C. and 99°-100° C., and solidify at 119° C. and 85°-86° C. respectively.[1]

Isoleic acid combines with hydriodic acid, forming an iodostearic acid which can be reduced to ordinary stearic acid by means of nascent hydrogen, and re-converted into isoleic acid by alcoholic potassium hydroxide. In like manner, the dibromide of isoleic acid reproduces isoleic acid on treatment with zinc and hydrochloric acid.

Stearidic Acid.—By the action of water on bromostearic acid (from bromination of stearic acid) *Oudemanns*[2] obtained an acid isomeric with oleic acid, together with silver bromide. This product distilled unchanged: melting point 35° C.

Two anhydrides of hydroxystearic acids are also known, isomeric with oleic acid—viz., *stearolactone*, γ-hydroxystearic "inner" anhydride (*q.v.*); and the body formed by the action of hydrochloric acid on α-hydroxystearic acid, regarded as—



$$C_{17}H_{34}\left\}\begin{matrix}CO\,.\,O\\O\,.\,CO\end{matrix}\right\{C_{17}H_{34}$$

Rapic Acid.—*Reimer* and *Will* separated from colza oil a liquid acid which they concluded to be isomeric with ricinoleic acid ($C_{18}H_{34}O_3$). The zinc salt melted at 78° C. *Zellner*,[3] however, has shown that this acid does not contain the third oxygen atom and that it is isomeric with oleic acid, from which it is distinguished by not giving the elaidin reaction.

PROPIOLIC (LINOLIC) GROUP OF FATTY ACIDS.

But few members of the group of acids of general formula $C_nH_{2n-3}\,.\,CO\,.\,OH$ have as yet been isolated from oils and fats, etc., the best known example being *linolic acid*, $C_{17}H_{31}\,.\,CO\,.\,OH$, contained in various drying oils, notably linseed oil. Several other members, however, have been produced from acids of the oleic series by employing the method founded on the same principle as that by means of which oleic acids are obtainable from acids of the acetic acid series—viz., by conversion into a chloro- or bromoderivative of an acetic acid and removal of the elements of HCl or HBr by the action of a base. Thus, oleic acid combined with Br_2 and the product treated with alcoholic potassium hydroxide furnishes *stearolic acid*[4]—

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[1] M. C. and A. Saytzeff, *J. prakt. Chem.*, 1888, xxxvii., 269.

[2] *J. prakt. Chem.*, 1863, lxxxix., 193.

[3] *Monatsh. f. Chem.*, 1896, xvii., 309; *J. Soc. Chem. Ind.*, 1896, xv., 661.

[4] According to Baruch (*Ber.*, 1894, xxvii., 172) the constitution of stearolic acid can be represented by the structural formula.

$$C_8H_{17}\,.\,C:C\,.\,[CH_2]\,.\,COOH.$$

$$\overset{\text{Oleic Acid.}}{C_{18}H_{34}O_2} + Br_2 = \overset{\text{Dibromostearic Acid.}}{C_{18}H_{34}Br_2O_2}$$

$$\overset{\text{Dibromostearic Acid.}}{C_{18}H_{34}Br_2O_2} - 2HBr = \overset{\text{Stearolic Acid.}}{C_{18}H_{32}O_2}$$

In similar fashion other homologues of stearolic acid (*e.g.*, *hendecolic palmitolic*, and *benolic* acids) can be prepared from the corresponding homologues of oleic acid, the general reaction being—

$$C_n H_{2n-2}Br_2O_2 - 2HBr = C_n H_{2n-4}O_2$$

In certain cases propiolic acids may be directly obtained from acids of the acetic family by treatment with chlorine or bromine, so as to produce dichloro- or dibromoderivatives of formula $C_n H_{2n-2}Br_2O_2$, which are then acted upon with alkalis so as to remove the elements of 2HBr, in accordance with the above equation; the total change produced being therefore equivalent to the removal of H_4. In this way, for instance, myristic acid, $C_{14}H_{28}O_2$, forms *myristolic acid*, $C_{14}H_{24}O_2$.

An analogous result is brought about with monochloro- or monobromoderivatives of acids of the acrylic series by similar treatment, the elements of HCl or HBr being removed, thus—

$$C_n H_{2n-3}ClO_2 - HCl = C_n H_{2n-4}O_2$$
$$C_n H_{2n-3}BrO_2 - HBr = C_n H^{2n-4}O_2$$

For instance, chlorocrotonic acid, $C_4H_5ClO_2$, gives rise by this treatment to *tetrolic acid*, $C_4H_4O_2$.

The table on p. 36 includes the chief acids of this series.

Absorption of Halogens.—Just as one molecule of an acrylic acid will combine with I_2 or Br_2, so will one of a propiolic acid unite with Br_4 or I_4, this action being substantially the reverse of that above described, where a dibromoacetic acid loses 2HBr and becomes a propiolic acid. The reaction is utilised in the practical testing of oils (Chap. VIII.).

Conversely, by the action of nascent hydrogen, zinc dust, and similar dechlorinising agents, the tetrabrominated or tetraiodised bodies thus formed become again reduced to the original propiolic acids. Thus linolic acid can be separated from accompanying acids (obtained by saponifying the mixture of glycerides contained in linseed oil, etc.) by combining with bromine, separating by crystallisation the tetrabrominated derivative, $C_{18}H_{32}Br_4O_2$ (melting at 114°-115° C.), and reproducing linolic acid by removing the bromine.

$$\overset{\text{Tetrabromostearic Acid.}}{C_{18}H_{32}Br_4O_2} - Br_4 = \overset{\text{Linolic Acid.}}{C_{18}H_{32}O_2}$$

Absorption of Oxygen.—Those propiolic acids that are formed by the bromine reaction above described (loss of 2HBr from dibromoderivatives of acids of the acetic group) possess the power of directly combining with oxygen (from suitable oxidising agents), forming saturated

Formula.	Name of Acid.	Melting Point.	Boiling Point.	Sources.
$C_3H_2O_2$	Propiolic,	...	...	Chloropropiolic acid, C_3HClO_2, is formed by the action of potassium hydroxide on dichloracrylic acid, $C_3H_2Cl_2O_2$.
$C_4H_4O_2$	Tetrolic,	76·5°	203°	Chlorocrotonic acid and potassium hydroxide.
$C_5H_6O_2$	Pentolic,	...	...	... ...
$C_6H_8O_2$	Sorbic,	Liquid at 15°	221°	Mountain ash berries.
	Parasorbic,	134·5°	...	
$C_7H_{10}O_2$	Benzoleic (Hydrobenzoic),	Liquid	...	Hydrogenation of benzoic acid.
$C_8H_{12}O_2$	Diallyl acetic,	Liquid	227°	Artificial.
$C_9H_{14}O_2$	...	...	...	... ...
$C_{10}H_{16}O_2$	Camphic,	...	...	Formed together with borneol by heating camphor with alcoholic sodium hydroxide.
	Campholenic,	...	Near 260°	Dibromcamphor and sodium amalgam.
$C_{11}H_{18}O_2$	Hendecolic (Undecolic or Hendecinoic),	59·5°	...	From undecylenic (hendecenoic) acid by bromine reaction.
$C_{12}H_{20}O_2$	... ...	...	...	... ...
$C_{13}H_{22}O_2$	... ...	...	...	... ...
$C_{14}H_{24}O_2$	Myristolic,	12°	...	From myristic acid by chlorination and action of alcoholic potassium hydroxide.
$C_{15}H_{26}O_2$	... ...	...	...	... ...
$C_{16}H_{28}O_2$	Palmitolic,	42°	...	From hypogæic acid by bromine reaction.
$C_{17}H_{30}O_2$	Elæomargaric,	48°	...	Tung oil.
	Elæostearic,	71°	...	Chinese wood oil.
$C_{18}H_{32}O_2$	Stearolic,	48°	...	From oleic acid by bromine reaction.
	Linolic,	Fluid	...	Linseed and other drying oils, maize oil, and most oils and fats.
	Ricilinolic,	Fluid	...	Dehydration of ricinoleic acid.
	Tariric,	50·5°	...	Seeds of tariri (genus *Picramnia*)
	Telfairic,	Fluid	220-225° (13 mm.)	Telfairia (kœme) oil.
$C_{19}H_{34}O_2$	... ...	...	...	... ...
$C_{20}H_{36}O_2$	... ...	Fluid	...	(?) Higher homologue of linolic acid, supposed to be contained in some drying oils.
$C_{21}H_{38}O_2$	... ...	...	...	... ...
$C_{22}H_{40}O_2$	Behenolic (or Benolic),	57·5°	...	From erucic acid, by bromine reaction.

compounds by the addition of two oxygen atoms instead of four bromine atoms, thus—

$$\begin{array}{lcccl} \text{Propiolic Acid.} & & & & \text{Saturated Compounds.} \\ C_nH_{2n-3}\,.\,CO\,.\,OH & + & Br_4 & = & C_nH_{2n-3}\left\{\begin{array}{l} Br_4 \\ CO\,.\,OH \end{array}\right. \\ C_nH_{2n-3}\,.\,CO\,.\,OH & + & O_2 & = & C_nH_{2n-3}\left\{\begin{array}{l} =O \\ =O \\ -CO\,.\,OH \end{array}\right. \end{array}$$

In this way stearolic acid, $C_{19}H_{32}O_2$, forms *stearoxylic* acid, $C_{18}H_{32}O_4$; and similarly with palmitolic and benolic acids. The general character of the action is indicated by the equation—

$$R\,.\,CH = CH\,.\,S\,.\,CH = CH\,.\,T + O_2 = R\,.\,\overset{\frown O \frown}{CH-CH}\,.\,S\,.\,\overset{\frown O \frown}{CH-CH}\,.\,T$$

Elæomargaric Acid.—This acid was discovered by *Cloez* in elæacocca oil (Tung Oil, *q.v.*), in which it occurs as a glyceride. It forms rhombic crystals which melt at 48° C., and when exposed to the air absorbs oxygen and forms a sticky mass. Its formula, according to *Cloez*, is $C_{17}H_{30}O_2$.

Linolic Acid.—The earlier researches on the acids derivable from the chief glycerides contained in linseed and other drying oils led to the conclusion that they were identical, and indicated by the formula $C_{16}H_{28}O_2$, and to this body the name *linoleic acid* was applied. Later experiments, however, have shown conclusively that a considerably higher molecular weight is possessed by the acid obtained from linseed oil, and have rendered it not improbable that different homologous acids exist (related as myristic, palmitic, and stearic acids, for example), and that different drying oils are not always identical as regards the leading acid of the series present. Linolic acid was originally obtained by *Schüler* by saponifying linseed oil with sodium hydroxide, salting out, dissolving in water, and precipitating with calcium chloride. The precipitate was treated with ether, whereby calcium linolate was dissolved out, leaving other substances undissolved. By agitating the ethereal solution with hydrochloric acid, and evaporating at a low temperature in an atmosphere of hydrogen, crude linolic acid was obtained. This was purified by treatment with alcoholic ammonia, precipitating as barium salt, and regenerating the acid as before. The analysis of the acid and its salts by *Schüler*, and subsequent investigators, led to the formula $C_{16}H_{28}O_2$.

On the other hand, the saponification values (Chap. VIII.) for linseed oil and other drying oils lead to the conclusion that the mean molecular weight of the fatty acids contained therein, is sensibly higher than 252, the value corresponding with $C_{16}H_{28}O_2$; the saponification equivalents for linseed, poppy, and hemp oils thus deduced mostly lie between 285 and 300, giving an average of 293 or thereabouts for the glycerides, and consequently of about 280 for the fatty acids which they contain ($C_{18}H_{32}O_2 = 280$). Further, various later analyses of linolates and other derivatives corroborate this formula; whilst *Peters*[1] obtained *stearic acid* (of melting point 69°) by hydrogenating linolic acid by means of strong hydriodic acid and phosphorus.

Still higher molecular weights result from the observations of some chemists. Thus *Allen*[2] found that whilst the linolic acids isolated from several different samples of linseed oil possessed mean equivalent weights varying between 282 and 295, another specimen, prepared with great care in an atmosphere of coal-gas, gave 307·2 ($C_{20}H_{36}O_2 = 308$). *Norton* and *Richardson*[3] found that linolic acid from linseed oil, when distilled at about 290° under a pressure of 89 mm., gave a colourless distillate, constituting about three-quarters of the whole; this was capable of being redistilled unchanged. It consisted of an acid of specific gravity 0·9108 at $\frac{15^\circ}{4^\circ}$ C., giving numbers on analysis corresponding with the formula $C_{20}H_{36}O_2$; the vapour density was found to be 153, this formula representing 154. Moreover, when heated with hydriodic acid it did not form stearic acid, melting at 69° C., as in the case of Peter's product, but an acid of considerably higher melting point—83° C. (arachidic acid, $C_{20}H_{40}O_2$, melts at 75° C.).

Reformatsky,[4] on repeating the experiments of Schüler, obtained from linseed oil freshly expressed in the laboratory a crude linolic acid that did *not* distil unchanged at 292° C. under 100 mm. pressure. It contained a considerable amount of oleic acid, yielding dihydroxystearic acid on oxidation with permanganate; by heating with alcohol and gaseous hydrochloric acid, *ethyl linolate* was ultimately obtained, distilling at 270°-275° C. under 180 mm. pressure; from this by saponification linolic acid was regenerated in a state of comparative purity —*e.g.*, giving the iodine number 172·65 to 180·3, that calculated being 181·4. When dissolved in glacial acetic acid the products thus prepared formed two compounds on addition of bromine—viz., a tetrabromide (addition product), $C_{18}H_{32}O_2Br_4$, as a viscid oil; and a crystallisable hexabrominated substance, regarded by him as a bromosubstitution derivative of the tetrabromide, $C_{18}H_{30}O_2Br_6$, melting at 177°-178° C. and solidifying at 175° C. Oxidation with alkaline permanganate yielded tetrahydroxystearic (*sativic*) acid and a little azelaic acid.

Whilst it appears exceedingly probable from the preceding results that more than one homologous acid of the series $C_n H_{2n-4}O_2$ exists in ordinary drying oils, it is more than doubtful whether any single substance in a state of purity was examined by any of the various observers, inasmuch as purification by recrystallisation of a well-marked crystalline derivative was not found readily practicable.

On the other hand, *Hazura* and *Grüssner* obtained from hemp-seed

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[1] *Monatsh. f. Chemie*, 1886, vii., 552.

[2] *Commercial Organic Analysis*, vol. ii., 1886, 117.

[3] *Ber.*, 1887, xx., 2735.

[4] *J. Soc. Chem. Ind.*, 1890, ix., 744; from *J. prakt. Chem.*, 1890, xli., 529.

oil[1] a mixture of fatty acids which on solution in acetic acid and treatment with bromine gave more than one brominated product of crystallisable character, as well as non-crystalline ones. One of the crystallisable products was found to melt at 177°-178° C., and to have the composition $C_{18}H_{30}O_2Br_6$; another melted at 114°-115° C., and had the composition $C_{18}H_{32}O_2Br_4$. From this latter by the action of zinc and alcoholic hydrochloric acid the bromine was removed, producing linolic acid, $C_{18}H_{32}O_2$, free from admixture with other acids. It was found impracticable to brominate the bromine compound, $C_{18}H_{32}O_2Br_4$, so as to obtain from it any substitution derivative, $C_{18}H_{30}O_2Br_6$; whence it appears that the hexabrominated body, melting at 177°-178° C., was *not* formed by the further substitutive action of bromine on the tetrabrominated addition product (as supposed by Reformatsky), but must have been produced by the direct combination of Br_6 with an acid, $C_{18}H_{30}O_2$, simultaneously present with linolic acid, etc., in the original mixture. This acid, *linolenic acid*, is in fact easily reproduced from the hexabromide by treatment with zinc and alcoholic hydrochloric acid so as to remove the bromine. Conversely, it is again converted into the original hexabromide by direct combination with Br_6.

Oxidation Products.—The linolic acid thus obtained from the tetrabromide of melting point 114°-115° C., $C_{18}H_{32}O_2Br_4$, reproduced that substance by combination with bromine; and similarly combined with I_4, but did not form a hexabrominated derivative; on oxidation with alkaline permanganate it formed a tetrahydroxystearic acid, *sativic acid*, $C_{18}H_{36}O_6 = C_{17}H_{31}\left\{\begin{matrix}(OH)_4\\ CO\,.\,OH\end{matrix}\right.$, together with a little azelaic acid and other secondary products, but no linusic acid. *Sativic acid* melts at 173°-174° C.[2] On heating with hydriodic acid and phosphorus, it forms an iodised acid, reduced to *stearic acid* by means of zinc and hydrochloric acid. It dissolves in 1,000 parts of *boiling* water, and is readily soluble in alcohol, but insoluble in *cold* water and in ether. By acetylation it forms a tetracetyl derivative, $C_{17}H_{31}\left\{\begin{matrix}(O\,.\,C_2H_3O)_4\\ CO\,.\,OH\end{matrix}\right.$; hence it obviously possesses the constitution of a quadruply hydroxylated stearic acid. On further oxidation it does not form linusic acid, but produces *azelaic acid*, $C_7H_{14}(CO\,.\,OH)_2$.

Hehner and *Mitchell*[3] repeated some of Hazura's work, and confirmed his statement as to the composition and properties of sativic acid obtained from the unsaturated fatty acids of maize oil. The melting point of their purest substance, however, was 114° C.

Isomerides of Linolic Acid.—*Stearolic acid*, obtained by combination of oleic acid with Br_2, and removing the elements of 2HBr from the product, fuses at 48°. By oxidation with alkaline permanganate, this forms *stearoxylic acid*, $C_{18}H_{32}O_4$, melting at 84°-86° C., together with some *suberic acid*, $C_6H_{12}(CO\,.\,OH)_2$, produced by the further

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[1] *J. Soc. Chem. Ind.*, 1888, 506; from *Monatsh. f. Chem.*, ix., 180.

[2] According to earlier observations, at 160°-162° C.

[3] *Analyst*, 1898, xxiii., 313.

oxidation of the stearoxylic acid first formed (*Hazura*). Nitric acid also directly oxidises it to stearoxylic acid, with formation also of *azelaic acid*, $C_7H_{14}(CO \cdot OH)_2$ (*Overbeck*), and of *pelargonic* (ennoic) acid (*Limpach*).

Tariric Acid.—A. Arnaud[1] described an acid isomeric with linolic acid contained as triglyceride in the seeds of "tariri," a shrub common in Guatemala; it melts at 50·5° C., and unites with bromine, forming a tetrabromide, $C_{18}H_{32}Br_4O_2$, melting at 125° C.

Telfairic Acid.—Another acid of the linolic series was isolated by *Thoms*[2] from Telfairia oil (Koeme oil). It solidifies at − 6° C., and boils at 220°-225° C. under a pressure of 13 mm. It forms a crystalline tetrabromide, and on oxidation with alkaline permanganate yields a tetrahydroxystearic acid, $C_{18}H_{32}O_2(OH)_2$, melting at 177° C.

Ricilinolic Acid.—This name may be conveniently applied to the acid obtained by *Krafft*[3] by heating ricinoleic acid under diminished pressure (15 mm.), when an acid distilled, liquid at ordinary temperature, but solidifying on chilling; this boiled at 230° C. at 15 mm.; and gave numbers indicating that it was an isomeride of linolic acid[4] produced by the dehydration of ricinoleic acid, which might be expected *a priori* to take place, thus—

Ricinoleic Acid. Dehydrated Derivative.

$$C_{17}H_{32}\left\{\begin{matrix}OH\\ CO \cdot OH\end{matrix}\right. = H_2O + C_{17}H_{31} \cdot CO \cdot OH$$

LINOLENIC GROUP OF FATTY ACIDS.

The existence in drying oils of two isomeric acids of formula $C_nH_{2n-5} \cdot CO \cdot OH$ (where $n = 17$) in the form of glycerides has been rendered extremely probable, if not conclusively substantiated, by *Hazura* and various collaborators. When the fatty acids isolated from such oils—*e.g.*, hemp-seed or linseed oil—are dissolved in acetic acid, at least three different brominated compounds are obtainable by the addition of bromine—viz., crystallisable *linolic acid tetrabromide*, $C_{16}H_{32}O_2Br_4$, melting at 114°-115° C., and the crystallisable hexabromide, $C_{18}H_{30}O_2Br_6$, melting at 177°-178° C., above described together with a non-crystallisable liquid bromide, apparently containing an isomeric hexabromide, $C_{18}H_{30}O_2Br_6$.

Linolenic Acid.—As already stated, the crystallisable hexabromide loses Br_6 by the action of zinc and alcoholic hydrochloric acid, forming *linolenic acid*, $C_{18}H_{30}O_2$, from which the same hexabromide can be reproduced by bromination, though, as *Hehner* and *Mitchell*[5] have

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[1] *Comptes Rendus*, cxiv., 79.

[2] *Arch. d. Pharm.*, 1900, ccxxxviii., 48.

[3] *Ber.*, 1888, 2730.

[4] By heating ricinoleic acid *in vacuo*, Norton and Richardson obtained an acid which closely resembled linolic acid, and was regarded by them as $C_{20}H_{36}O_2$ (*Ber.*, 1887, xx., 2735).

[5] *Analyst*, 1898, xxiii., 313.

shown, the yield is by no means quantitative (only 46-50 per cent. of the theoretical amount of bromine being taken up), this being due to rapid oxidation of the free acid. By oxidation with alkaline permanganate no sativic acid is produced, but, instead, *linusic acid*, a hexahydroxystearic acid, $C_{17}H_{29}\left\{\begin{matrix}(OH)_6\\ CO\,.\,OH\end{matrix}\right.$. This last melts at 203°-205° C., and furnishes a hexacetyl derivative, $C_{17}H_{29}\left\{\begin{matrix}(O\,.\,C_2H_3O)_6\\ CO\,.\,OH\end{matrix}\right.$. Hence the pre-existence of linolenic acid in the original mixture of acids, as the source of the crystallisable hexabromide, would seem to be pretty clearly demonstrated.

Hehner and *Mitchell* (*loc. cit.*) prepared from linseed oil fatty acids the insoluble hexabromide containing 61·80 per cent. of bromine as compared with the theoretical quantity 63·31, and melting at 180°-181° C. (Hazura, 177° C.).

On boiling this with alcoholic potassium hydroxide the bromine was completely eliminated, and on liberating the acids from the potassium salt a yellow viscid oil absorbing 61-63 per cent. of iodine was obtained.

The linolenic acid prepared by Hazura rapidly underwent oxidation and could not be obtained in a pure state, so as to absorb more than 245 per cent. of iodine as against the theoretical quantity 274·1 per cent. In Hehner and Mitchell's experiments the iodine absorption of the linolenic acid was 241·8, and the acid, which was a nearly colourless liquid, had a specific gravity of 0·9228 at 15·5° C. (compared with water at the same temperature). It absorbed oxygen from the air with great avidity, and speedily became dark brown.

Isolinolenic Acid.—The existence of an isomeric modification of linolenic acid, *isolinolenic acid*, is inferred from the fact of a non-crystalline hexabromide being apparently produced by the addition of bromine to the original mixed acids, together with the circumstance that on oxidising the mixture by alkaline permanganate there are formed (in various relative proportions, according to the kind of drying oil operated on) not only *dihydroxystearic acid* (from oleic acid), *sativic acid* (tetrahydroxystearic acid, due to linolic acid, $C_{18}H_{32}O_2$), and *linusic acid* (due to linolenic acid), but also another hexahydroxylated stearic acid, *isolinusic acid*, isomeric with linusic acid. This melts at 173°-175° C., and furnishes a hexacetyl derivative, $C_{17}H_{29}\left\{\begin{matrix}(O\,.\,C_2H_3O)_6\\ CO\,.\,OH\end{matrix}\right.$, resembling that obtained from linusic acid, but being less soluble in ether.

The tables on next page show the amounts of hydroxy derivatives obtained by *Hazura* and *Grüssner* from various oils, and the approximate composition of the unsaturated acids calculated from these results.

It will be observed that the yields of hydroxy derivatives were far from being quantitative, and that there must have been considerable destruction of the first products of oxidation, especially of those derived from the least saturated products.

	100 Grammes of Liquid Fatty Acids yielded				
	Linseed.	Hemp.	Nut.	Poppy.	Cotton.
Dihydroxystearic acid, . .	1·2	4·0	2·5	8·5	23·0
Sativic acid, ...	6·5	24·0	25·0	18·5	31·5
Linusic + isolinusic acids, .	20·3	2·5	2·0	0·3	...
Grammes, . .	28·0	30·5	29·5	27·3	54·5

	Approximate Percentage Composition of Liquid Fatty Acids.				
	Linseed.	Hemp.	Nut.	Poppy.	Cotton.
Oleic acid, ...	5	15	7	30	40
Linolic acid, ...	15	70	80	65	60
Isolinolenic acids, . .	15	15	13	5	0
Linolenic acids, . .	65				

It was shown by *Hehner* and *Mitchell*[1] that the linolenic acid obtained by reducing the hexabromide from linseed oil fatty acids yields only a small amount of hexabromide when again brominated. *Erdmann* and *Bedford*[2] attributed this to the linolenic acid thus obtained, consisting of two stereo-isomeric acids, which they termed α- and β-linolenic acids, and regarded as analogous to oleic and elaidic acids.

According to their theory the α-linolenic acid is identical with that present in the original linseed oil fatty acids, and yields the solid hexabromide on bromination, whilst the β-modification absorbs by addition only four atoms of bromine to form a fluid tetrabromide, $C_{18}H_{30}Br_4O_2$. The linolenic acid reduced from the hexabromide yields on treatment with ozone two ozonides, $C_{18}H_{30}O_{11}$, or ozonide peroxides, $C_{18}H_{30}O_{12}$, whilst the ethyl esters form ozonides, having the composition, $C_{30}H_{34}O_2$ (or $C_{30}H_{34}O_{12}$), which may be distinguished from one another by the difference in their solubility in water, that corresponding with the α-linolenic acid being more readily soluble. The linolenic acid from linseed oil fatty acids has, therefore, the following constitutional formula (*Erdmann*, *Bedford*, and *Raspe*).[3]

$$CH_3 \,.\, CH_2 \,.\, CH : CH_2 \,.\, CH : CH \,.\, CH_2 \,.\, CH \cdot CH \,.\, CH_2 \,.\, CH_2 \,.\, COOH.$$

Rollett[4] subjected this theory to a critical examination. The linolenic acid prepared by him by reduction of the hexabromide had an iodine value of 267·4 (theory = 274·2) and a specific gravity of 0·9141 at 18°-4° C. (that of the acid prepared by Hehner and Mitchell being 0·9228 at 15° C.). When brominated this absorbed six atoms of bromine, yielding about 20 per cent. of solid hexabromide and 80 per cent. of a crude fluid tetrabromide, which was slowly converted by further

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[1] *Analyst*, 1899, xxiv., 77.

[2] *Ber.*, 1909, xlii., 1324.

[3] *Ibid.*, 1334.

[4] *Zeit. physiol. Chem.*, 1909, lxii., 422.

bromination into a fluid hexabromide. The latter when reduced with hydrogen yielded a linolenic acid, which by rebromination gave a further deposit of solid hexabromide. When pure linolenic acid was oxidised it yielded both the linusic and isolinusic acids of Hazura. Hence the conclusion was drawn that there is insufficient proof of the existence of either Hazura's isolinolenic acid or of Erdmann's β-linolenic acid. Theoretically four additional bromides are obtainable from linolenic acid, and the fact that the experimental yields of solid hexabromide are invariably less than 25 per cent. is what might be expected.

In reply to these criticisms *Erdmann* and *Bedford*[1] pointed out that the liquid fatty acids of the linseed oil examined by them had an iodine value of 203·8, whilst the theoretical amount of linolenic acid obtainable from a mixture of linolic and linolenic acids with that iodine value would be 24·4 per cent. The balance of the chemical evidence appears to support Erdmann's theory of two isomeric linolenic acids.

Jecoric Acid.—*Fahrion*[2] was the first to infer that an acid of the same elementary composition as linolenic acid ($C_{18}H_{30}O_2$) was present in sardine oil, his deductions being drawn from the analysis of the barium, calcium, and magnesium salts. When oxidised with alkaline permanganate, by Hazura's method it does not yield a hydroxylated acid, but only carbon dioxide and volatile acids. It is not improbable, however, that this may be due to its being so much more readily oxidised than linolenic acid.

Considerable doubt was subsequently thrown on Fahrion's conclusions, but the experiments of *Hehner* and *Mitchell*[3] afforded corroborative evidence of their correctness.

The free fatty acids of cod-liver oil yielded, on bromination, a white precipitate, which, when dried in the water-oven, became dark brown. This contained 62·91 per cent. of bromine, whilst the theoretical quantity for the hexabromide of jecoric acid would be 63·31 per cent. The air-dried substance decomposed below 200° C. without having melted. A similar compound was obtained from whale, shark, and other marine animal oils.

ACIDS OF THE CLUPANODONIC SERIES $C_nH_{2n-8}O_2$.

Acid in Cod-Liver Oil.—*Möller*[4] isolated from the fatty acids of cod-liver oil a compound to which he assigned the formula $C_{18}H_{28}O_2$.

This was probably the same fatty acid which was subsequently isolated by *Tsujimoto*[5] from the mixed acids of Japanese sardine oil, by reduction of an octobromide. It was a liquid with an iodine value of 344 (theory = 368), and was given the name of clupanodonic acid.

Acid, $C_{20}H_{32}O_2$.—*Bull*[6] also isolated from cod-liver oil and other marine animal oils a liquid acid with the formula $C_{20}H_{32}O_2$. His

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[1] *Ibid.*, 1910, lxix., 76.

[2] *J. Soc. Chem. Ind.*, 1893, xii., 938.

[3] *Loc. cit.*

[4] *Cod-liver Oil and Chemistry.*

[5] *J. Coll. Eng., Tokyo*, 1906, iv. 1.

[6] *Chem. Zeit.*, 1899, xxiii., 996, 1043.

method of separation was based on the ready solubility of the sodium salts of the more unsaturated fatty acids in ether. The cod-liver (torsk) oils, with the exception of those from Japanese fish, contained from 12-21 per cent. of fatty acids belonging to this series; whale oils contained from 4-19 per cent., and sardine oils from 14-26 per cent.

In herring oil two unsaturated liquid acids, solidifying below $-20°$ C., and having the formulæ $C_{20}H_{32}O_2$ and $C_{24}H_{40}O_2$, were discovered.

Isanic Acid.—An unsaturated acid with the formula $C_{14}H_{20}O_2$ was obtained by *Hebert*[1] from the oil of I'Sano seed. It formed foliated crystals which melted at 41° C.

ACIDS OF SERIES $C_n H_{2n-10}O_2$.

Acid $C_{23}H_{26}O_2$ (?).—Unsaturated liquid acids belonging to this series, one of which was believed to have the composition $C_{23}H_{36}O_2$, were separated by *Bull* (*loc. cit.*) by his method of treating the sodium salts of the unsaturated fatty acids of various marine animal oils with ether.

HYDROXYACETIC (GLYCOLLIC) GROUP OF FATTY ACIDS.

The members of this group $\left(\text{general formula, } C_mH_{2m}\left\{\begin{matrix}OH\\CO\,.\,OH\end{matrix}\right.\right)$ hitherto recognised as normal constituents of fats, oils, waxes, etc., are but few in number. Carnauba wax has been found by *Stürcke*[2] to contain a small quantity of a substance simultaneously possessing the properties of an alcohol and an acid, indicated by the formula $C_{19}H_{38}\left\{\begin{matrix}CH_2\,.\,OH\\CO\,.\,OH\end{matrix}\right.$. When this is heated with soda lime, it forms an acid of the oxalic family with evolution of hydrogen.

$$C_{19}H_{38}\left\{\begin{matrix}CH_2\,.\,OH\\CO\,.\,OH\end{matrix}\right. + 2NaOH = C_{19}H_{38}\left\{\begin{matrix}CO\,.\,ONa\\CO\,.\,ONa\end{matrix}\right. + 2H_2 + H_2O$$

Hydroxymyristic Acid.—The essential oil of *Angelica archangelica* contains (probably as some form of compound ester) an acid which appears to be *hydroxymyristic acid*,[3] $C_{13}H_{26}\left\{\begin{matrix}OH\\CO\,.\,OH\end{matrix}\right.$, melting at 51° C., and yielding a *benzoyl-hydroxymyristic acid*, $C_{13}H_{26}\left\{\begin{matrix}O\,.\,C_6H_5O\\CO\,.\,OH\end{matrix}\right.$, melting at about 68° C. A hydroxymyristic acid apparently identical with this is obtainable from myristic acid by brominating and treating the resulting monobromomyristic acid with caustic soda.

Hydroxypalmitic and Hydroxystearic Acids.—By similar processes palmitic acid yields *hydroxypalmitic acid* and stearic acid, *hydroxy-*

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[1] *Bull. Soc. Chim.*, 1896, xv., 941.

[2] *Annalen der Chem.*, cciii., 283; also *J. Soc. Chem. Ind.*, 1884, iii., 448.

[3] R. Müller, *Ber.*, 1881, xiv., 2476.

stearic acid. Of this latter body, moreover, more than one isomeric modification is known. Thus *M. C.* and *A. Saytzeff*[1] found that *α-hydroxystearic acid* was obtained when isoleic acid (m.p. 45°) was combined with hydriodic acid so as to form an iodostearic acid, and the product treated with silver hydroxide; whilst *β-hydroxystearic acid* was similarly obtained from ordinary oleic acid; the reaction in each case being expressed by the equations

$$\overset{\text{Oleic Acid.}}{C_{18}H_{34}O_2} + HI = \overset{\text{Iodostearic Acid.}}{C_{18}H_{35}IO_2}$$

$$\overset{\text{Iodostearic Acid.}}{C_{18}H_{35}IO_2} + AgOH = AgI + \overset{\text{Hydroxystearic Acid.}}{C_{18}H_{35}(OH)O_2}$$

α-hydroxystearic acid melts at 80°-82° C., and distils unchanged; whilst β-hydroxystearic acid breaks up on heating into water and ordinary oleic acid—

$$\overset{\text{Hydroxystearic Acid.}}{C_{18}H_{35}(OH)O_2} = H_2O + \overset{\text{Oleic Acid.}}{C_{18}H_{34}O_2}$$

The same two acids can also be obtained by treating isoleic acid with sulphuric acid, when combination takes place with the formation of two isomeric hydroxystearosulphuric acids, which by the hydrolytic action of water are decomposed into sulphuric acid and hydroxystearic acids, thus—

$$\overset{\text{Isoleic Acid.}}{C_{17}H_{33} . CO . OH} + \overset{\text{Sulphuric Acid.}}{H_2SO_4} = \overset{\text{Hydroxystearo-sulphuric Acid.}}{C_{17}H_{34}\left\{\begin{matrix} O . SO_3H \\ CO . OH \end{matrix}\right.}$$

$$\overset{\text{Hydroxystearo-Sulphuric Acid.}}{C_{17}H_{34}\left\{\begin{matrix} O . SO_3H \\ CO . OH \end{matrix}\right.} + \overset{\text{Water.}}{H_2O} = \overset{\text{Hydroxystearic Acid.}}{C_{17}H_{34}\left\{\begin{matrix} OH \\ CO . OH \end{matrix}\right.} + \overset{\text{Sulphuric Acid.}}{H_2SO_4}$$

the two reactions jointly are consequently tantamount to the addition of water to isoleic acid—

$$\overset{\text{Isoleic Acid.}}{C_{15}H_{31} - CH = CH - CO . OH} + H_2O \overset{\text{Hydroxystearic Acid.}}{\left\{\begin{matrix} = C_{15}H_{31} - CH_2 - CH . OH - CO . OH \\ = C_{15}H_{31} - CH . OH - CH_2 - CO . OH \end{matrix}\right.}$$

The α- or the β-acid thus results according as the hydroxyl group becomes added to the penultimate or antepenultimate carbon.

Stearolactone.—*Geital*[2] found that when ordinary oleic acid is thus treated with sulphuric acid, besides the α-hydroxystearic acids above described a *γ-hydroxystearic acid*, $C_{14}H_{29} - . CH . OH - CH_2 - CH_2 - CO . OH$, is produced, which readily forms an "inner" anhydride, *stearolactone*, $C_{14}H_{29} - \overbrace{CH - CH_2 - CH_2 - CO}^{O}$. This anhydride is produced whenever a salt of γ-hydroxystearic acid is decomposed by a mineral acid. If the acid solution is cautiously neutralised in the cold by an alkali, the stearolactone remains unaltered, and may be obtained by dissolving out with ether or petroleum spirit, and thus separated from any other accompanying fatty acids set free by the

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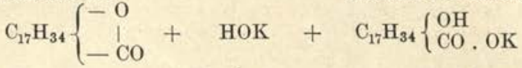
[1] *Jahresbericht*, 1888, 1916; from *J. prakt. Chem.*, [2], xxxvii., 269.

[2] *J. Soc. Chem. Ind.*, 1888, vii., 218; from *J. prakt. Chem.*, [2], xxxvii., 53.

mineral acid, but retained by the subsequent addition of alkali. When boiled with alcoholic potassium hydroxide, however, potassium γ-hydroxystearate is produced.

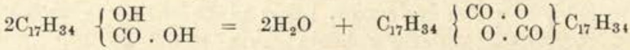


Stearolactone. Potassium Hydroxystearate.

$$C_{17}H_{34}\left\{\begin{array}{l}-\,O\\ \;\;|\\ -\,CO\end{array}\right. + \quad HOK \quad + \quad C_{17}H_{34}\left\{\begin{array}{l}OH\\ CO\,.\,OK\end{array}\right.$$

Processes for detecting and estimating stearolactone in mixture with free fatty acids, etc., are founded on these reactions. Stearolactone is readily soluble in alcohol, ether, and light petroleum spirit. It crystallises in needles melting at 51° C. It is formed in somewhat large quantity when oleic acid is heated with zinc chloride and the product treated with water (*Benedikt*), probably by reactions analogous to those taking place under the influence of sulphuric acid (*vide* Chap. VII.).

An anhydride isomeric with stearolactone is formed by the action of hydrochloric acid upon α-hydroxystearic acid (*C.* and *A. Saytzeff*) in accordance with the equation—



$$2C_{17}H_{34}\left\{\begin{array}{l}OH\\ CO\,.\,OH\end{array}\right. = 2H_2O + C_{17}H_{34}\left\{\begin{array}{c}CO\,.\,O\\ O\,.\,CO\end{array}\right\}C_{17}H_{34}$$

This substance is fluid at the ordinary temperature and does not solidify on chilling; it combines with neither bromine nor iodine (Hübl's reagent), but on heating with potassium hydroxide becomes wholly converted into potassium hydrostearate; on acidifying the product, α-hydroxystearic acid is set free, and not an anhydride, as in the case of stearolactone.

HYDROXYACRYLIC (RICINOLEIC) GROUP OF FATTY ACIDS.

Ricinoleic Acid.—The acids of general formula $C_n\,H_{2n-2}\left\{\begin{array}{l}OH\\ CO\,.\,OH\end{array}\right.$ obtained by the saponification of fixed oils, etc., are represented by *ricinoleic acid*, $C_{17}H_{32}\left\{\begin{array}{l}OH\\ CO\,.\,OH\end{array}\right.$, the only one as yet known with certainty. Castor oil, and to a less extent some other oils, contain ricinolein, the glyceride of ricinoleic acid. To isolate the acid, castor oil is saponified with concentrated potassium hydroxide solution, and the resulting soap decomposed by heating for a short time with hydrochloric acid. The separated acids are washed with water several times, and then cooled to 0° C., or somewhat lower; the mass solidifies and is subjected to pressure, first gentle then stronger, so as to squeeze out fluid substances, the temperature being gradually raised to 10°-12° C. If any considerable quantity of unsaponified oil is mixed with free fatty acids, their solidification by chilling is greatly hindered, a result also brought about by the presence of bye-products formed by the action of the air on the free fatty acids; wherefore the saponifying and decomposing operations, etc., should be conducted as rapidly as possible. As thus purified ricinoleic acid melts at 16°-17° C., the phenomenon of superfusion being strongly shown by the liquid acid, which usually does not solidify until considerably chilled.

When castor oil is heated, the ricinoleic acid present as glyceride breaks up into œnanthol and hendecenoic acid, thus—

$$\overset{\text{Ricinoleic Acid.}}{C_{18}H_{34}O_3} = \overset{\text{Œnanthol.}}{C_7H_{14}O} + \overset{\text{Hendecenoic Acid.}}{C_{11}H_{20}O_2}$$

Free ricinoleic acid, however, when heated does not split up in this way at all, neither does it distil unchanged even under greatly diminished pressure—below 15 mm. An acid distillate passes over at about 250° C., which on rectification furnishes an acid boiling at about 230° C. at 15 mm.; and giving numbers corresponding with the formula $C_{18}H_{32}O_2$, whence it would seem that water is thus split off from ricinoleic acid yielding a linolic acid isomeride.

Hydriodic acid and phosphorus acting in the presence of iodine convert ricinoleic acid into di-iodostearic acid, $C_{18}H_{34}I_2O_{21}$, which, when reduced with nascent hydrogen, yields stearic acid, and when boiled with alcoholic potassium hydroxide is converted into the salt of an acid isomeric with linolic acid. Heating with potassium hydroxide forms a secondary decyclic alcohol, $C_{10}H_{21}(OH)$, and sebacic acid, $C_8H_{16}(CO.OH)_2$, from which reactions the structure $CH_3 - (CH_2)_5 - CH.OH - CH = CH - (CH_2)_8 - CO.OH$ would seem probable. Alkaline permanganate oxidises ricinoleic acid to trihydroxystearic acid (*Dieff* and *Reformatsky*).

Ricinelaidic Acid.—By the action of nitrous acid ricinoleic acid is converted into *ricinelaidic acid* melting at 52°-53° C.; on heating under diminished pressure, this is decomposed much more slowly than ricinoleic acid. Oxidation by means of nitric acid readily converts it into normal *heptoic acid*, whilst alkaline permanganate induces the formation of trihydroxystearic acid.

Isoricinoleic Acid.—According to *Hazura* and *Grüssner*, two different trihydroxystearic acids are formed when ricinoleic acid is thus oxidised, respectively melting at 140°-142° C. (*trihydroxystearic acid*), and at 110°-111° C. (*isotrihydroxystearic acid*); from which they infer the presence in castor oil of two isomeric acids (*ricinoleic* and *isoricinoleic* acids respectively). Both of these trihydroxy acids form triacetyl derivatives, $C_{17}H_{32}\left\{\begin{matrix}(O.C_2H_3O)_3\\ CO.OH\end{matrix}\right.$; and both can be reduced to ordinary stearic acid by means of hydriodic acid. The isoricinoleic acid is present to the extent of about twice as much as the ricinoleic acid.

An isoricinoleic acid has also been described by *Jouillard*[1] (*vide infra*).

Polyricinoleic Acids.—According to *Meyer*,[2] the formation of complex polyricinoleic acids from ricinoleic acid occurs at ordinary temperatures without the agency of condensing agents. Thus a specimen of pure ricinoleic acid eight years old showed 30 to 40 per cent. less

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[1] *Bull. Soc. Chim.*, xiii., 238.

[2] *Zeit. angew. Chem.*, 1897, 297.

acidity than the original acid. These poly-acids were completely saponified (*i.e.*, re-converted into ricinoleic acid after twenty-four hours' treatment with hot potassium hydroxide solution).

Isomerides of Ricinoleic Acid.—On heating barium ricinoleate *Krafft* obtained a residue from which an acid termed by him *ricinic acid* was isolated,[1] apparently isomeric with ricinoleic acid; this melted at 81° C., and distilled unchanged at 250°-252° C. under 15 mm. pressure; by oxidation it yielded normal heptoic acid.

Hydroxyoleic Acid.—When the dibromide of oleic acid (dibromostearic acid) is treated with silver hydroxide it forms hydroxyoleic acid, apparently in consequence of the removal of the elements of HBr, forming bromoleic acid, and the action thereon of silver hydroxide, thus—

$$\underset{\text{Bromoleic Acid.}}{C_{17}H_{32}Br.CO.OH} + AgOH = AgBr + \underset{\text{Hydroxyoleic Acid.}}{C_{17}H_{32}\left\{\begin{matrix}OH\\CO.OH\end{matrix}\right.}$$

The same product results by first converting the dibromide into bromoleic acid by means of potassium hydroxide and then acting upon this with silver hydroxide (*Overbeck*). Hydroxyoleic acid is a thick liquid at ordinary temperatures but solidifies on chilling; by boiling with potassium hydroxide it takes up water, forming a *dihydroxystearic acid*, melting at 126° C.[2]

$$C_{17}H_{32}\left\{\begin{matrix}OH\\CO.OH\end{matrix}\right. + H_2O = C_{17}H_{33}\left\{\begin{matrix}(OH)_2\\CO.OH\end{matrix}\right.$$

In similar fashion, *hydroxyhypogæic acid*, $C_{15}H_{28}\left\{\begin{matrix}OH\\CO.OH\end{matrix}\right.$, is formed when the dibromide of hypogæic acid is treated with silver hydroxide (*Schröder*); as with oleic dibromide, the action probably takes place in two stages, the elements of HBr being first removed, forming bromohypogæic acid, $C_{16}H_{29}BrO_2$, and this being then converted into the hydroxy acid, thus—

$$C_{15}H_{28}Br.CO.OH + AgOH = AgBr + C_{15}H_{28}\left\{\begin{matrix}OH\\CO.OH\end{matrix}\right.$$

It melts at 34° C., and by boiling with potassium hydroxide solution takes up the elements of water forming *dihydroxypalmitic acid*, $C_{15}H_{29}\left\{\begin{matrix}(OH)_2\\CO.OH\end{matrix}\right.$, fusing at 115° C.

When oleic acid is heated to 200° C. and a stream of air blown through (as in the preparation of "blown oils," it absorbs oxygen and becomes largely converted into a *hydroxyoleic* acid (*Benedikt* and *Olzer*). The relationships of the oxidised oleins and similar substances contained in blown oils to ricinoleic glyceride (castor oil) have not been fully studied, but apparently there is a considerable degree of similarity between them. The same remark applies to the oxidised acids

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[2] Later experiments by Saytzeff indicate that this acid is identical with the dihydroxystearic acid melting at 136·5° C. obtained by him on oxidation of oleic acid with alkaline permanganate.

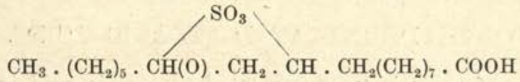
[1] *Ber.*, 1888, xxi., 2730.

formed when oils and fats are kept for long periods of time, so as to absorb a large proportion of oxygen from the air spontaneously.

On the other hand, when drying oils are exposed to the air in thin films, so as to " dry " up to solid varnishes, they absorb oxygen ; when the absorption attains its maximum, the increment in weight is tolerably close to that corresponding with the weight of iodine capable of being taken up by the original oil, whilst the capacity for absorbing iodine decreases *pari passu* with the oxidation.

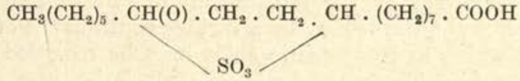
It would, therefore, seem that the tendency of atmospheric oxidation of drying oils is to produce less " unsaturated " oxidation products than the original substances ; whence by analogy in the case of oleic glyceride, it would seem probable that saturated acids are formed thus, rather than unsaturated acids like hydroxyoleic acid.

Action of Sulphuric Acid on Ricinoleic Acid.—Sulphuric acid reacts with ricinoleic acid to form sulphonated acids, the isomeric forms of which have the following formulæ :—



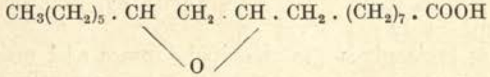
$$CH_3 . (CH_2)_5 . \overset{SO_3}{\overbrace{CH(O) . CH_2 . CH}} . CH_2(CH_2)_7 . COOH$$

and

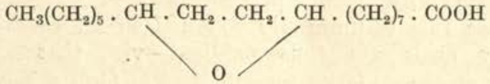


$$CH_3(CH_2)_5 . \underset{SO_3}{\underbrace{CH(O) . CH_2 . CH_2 . CH}} . (CH_2)_7 . COOH$$

According to *Chonowsky*,[1] when these sulpho-acids are boiled with water they are decomposed into sulphuric acid and the two isomeric glyceridic acids—



$$CH_3(CH_2)_5 . \underset{O}{\underbrace{CH \quad CH_2 . CH}} . CH_2 . (CH_2)_7 . COOH$$



$$CH_3(CH_2)_5 . \underset{O}{\underbrace{CH . CH_2 . CH_2 . CH}} . (CH_2)_7 . COOH$$

The first of these can be converted by potassium hydroxide into a dihydroxystearic acid.

These conclusions stand in need of confirmation, since they differ from results obtained by previous workers. They have been criticised by *Grün*, who found that the dihydroxystearic acid described by *Juillard* as one of the products of the reaction, was really a mixture of three isomeric dihydroxystearic acids melting respectively at 69·5°, 90°, and 108° C., whilst a fourth isomeride melting at 126° C. was subsequently isolated.

In the formation of these dihydroxystearic acids inner esters of the type $C_{17}H_{33}(OH)_2 . CO . O . C_{17}H_{33}(OH) COOH$ are produced as

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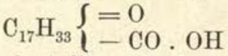
[1] *Ber.*, 1909, xlii., 3339 ; *ibid.*, 3759.

intermediate products, and it is possible that Chonowsky's "glycidic" acids consisted of these products or of a mixture of them with dihydroxystearic acids.

A product introduced into the market under the name of "oxyoleate," for use as a "Turkey red oil," is obtained by the action of sulphuric acid on certain oils, and decomposition of the compound sulphuric acid formed by heat (*vide* Chap. VII.).

Anhydrodioxystearic Acid.—When dihydroxystearic acid (melting point 136·5° C.) is distilled under diminished pressure (100 to 180 mm.) it breaks up into water, and a monobasic acid, isomeric with ricinoleic acid, melting at 77°-79° C., and solidifying at 66°-69° C.[1] From its mode of formation this product is obviously indicated by the formula,



$C_{17}H_{33}\left\{\begin{array}{l}=O\\-CO\,.\,OH\end{array}\right.$ being a saturated compound, not containing alcoholiform hydroxyl like ricinoleic acid.

POLYHYDROXYLATED STEARIC ACIDS.

A number of acids is known, related to stearic acid in that they are derived therefrom by the replacement of two or more hydrogen atoms by hydroxyl groups—*i.e.*, by a further continuance of the action by means of which hydroxystearic acids may be regarded as derived from stearic acid. These polyhydroxylated derivatives are all expressed by the general formula $C_{17}H_{35-n}(OH)_n\,.\,CO\,.\,OH$. When $n = 1$, some modification of hydroxystearic acid results; when $n = 2$, a dihydroxystearic acid (higher homologue of glyceric acid); similarly, when $n = 3$, 4, or 6, trihydroxy, tetrahydroxy, and hexahydroxystearic acids respectively result.

The following table gives the principal sources and melting points of these acids, the usual mode of production being gentle oxidation of the acid in question with alkaline permanganate.[2]

A remarkable rule is uniformly followed in all cases where unsaturated fatty acids are thus oxidised—viz., that *a number of hydroxyl groups is always taken up sufficient to form a saturated polyhydroxy acid.*[3] Thus in the case of the hydroxystearic acids, unsaturated acids of the formula $C_{17}H_{33}\,.\,CO : OH$ (oleic, isoleic, and elaidic acids), take up *two* hydroxyl groups forming three different dihydroxy-

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[1] A. Saytzeff, *J. prakt. Chem.*, [2], xxxiii., 300.

[2] A dihydroxystearic acid (melting point 136° C.) is also obtainable in small quantity by the action of silver hydroxide on the dibromide of oleic acid; also by the hydration of hydroxyoleic acid (*vide supra*). Hydroxyhypogæic acid (from dibromide of hypogæic acid) behaves similarly, forming a *dihydroxypalmitic acid*, melting point 115° C. A dihydroxypalmitic acid was obtained by Gröger (*inter alia*) by the direct oxidation of palmitic acid with alkaline permanganate. Two *dihydroxybenic acids* are known, respectively derived from the dibromides of erucic and brassic acids, and melting at 132°-133° and 98°-99° C.

[3] Hazura and Grüssner, *J. Soc. Chem. Ind.*, 1888, vii., 506; from *Monatsh. f. Chem.*, ix., 180.

Name.	Formula.	Source.	Melting Point.	Solidifying Point.
Dihydroxystearic acid,	$C_{17}H_{33}(OH)_2$ CO.OH,	Oleic acid,	136·5° C.	119°-122° C.
Isodihydroxystearic acid,	Do.,	Elaidic acid,	99°-100°	85°-86°
Do.,	Do.,	Isoleic acid,	77°-78°	64°-66°
Trihydroxystearic acid,	$C_{17}H_{32}(OH)_3$.CO.OH,	Castor oil,	140°-142°	...
Isotrihydroxystearic acid,	Do.,	Do.,	110°-111°	...
β-isotrihydroxystearic acid,	Do.,	Ricinelaidic acid,	114°-115°	...
Sativic acid (Tetrahydroxystearic acid),	$C_{17}H_{31}(OH)_4$.CO.OH,	Linolic acid,	173°-174°	...
Linusic acid (Hexahydroxystearic acid),	$C_{17}H_{29}(OH)_4$.CO.OH,	Linolenic acid,	203°-205°	...
Isolinusic acid (Isohexahydroxystearic acid)	Do.,	Hemp-seed oil, &c., (supposed isolinolenic acid),	173°-175°	...

stearic acids, $C_{17}H_{33}\left\{\begin{array}{l}(OH)_2\\ CO\,.\,OH\end{array}\right.$ Similarly ricinoleic and ricinelaidic acids, $C_{17}H_{32}\left\{\begin{array}{l}OH\\ CO\,.\,OH\end{array}\right.$, take up 2 hydroxyl groups, producing two trihydroxystearic acids, $C_{17}H_{32}\left\{\begin{array}{l}(OH)_3\\ CO\,.\,OH\end{array}\right.$ In the same way hendecenoic, hypogæic, and erucic acids take up 2 hydroxyl groups giving rise to dihydroxyhendecoic, dihydroxypalmitic, and dihydroxybenic acids respectively. On the other hand, linolic acid, $C_{17}H_{31}\,.\,CO\,.\,OH$, takes up 4 hydroxyl groups, producing sativic (tetrahydroxystearic) acid, $C_{17}H_{31}\left\{\begin{array}{l}(OH)_4\\ CO\,.\,OH\end{array}\right.$; whilst linolenic acid, $C_{17}H_{29}\,.\,CO\,.\,OH$, takes up 6 groups, producing linusic (hexahydroxystearic acid),

$$C_{17}H_{29}\left\{\begin{array}{l}(OH)_6\\ CO\,.\,OH\end{array}\right.$$

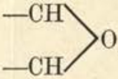
The above rule appears to be only a particular case of a considerably wider principle applying also to hydrocarbons and alcohols, etc., of unsaturated character, which may be put in the form of the following theorem :—

With substances containing the group $-\,CH = CH\,-$ (or certain groups thence derived, $-\,CR = CH,\,-$ and $-\,CR = CS\,-$, where R and S are monad alkyl radicles), *the effect of oxidising agents of not too energetic a character is to cause the addition of two hydroxyl radicles so as to form the group* $-\,CH\,.\,OH - CH\,.\,OH\,-$ (or the derived group

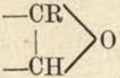
$- CR . OH - CS . OH -$), *this action occurring twice over if two groups* $- CH = CH -$ *are present; thrice over if three groups are present; and so on.*

Thus *Wagner* found[1] that olefines were readily transformed into glycols by means of potassium permanganate in virtue of this reaction; alcohols of unsaturated character (allylic series) similarly became glycerols; hydrocarbons containing the group $- CH = CH -$ twice (*e.g.*, diallyl) became erythrols, and so on. Glycerol itself is thus obtainable from allylic alcohol.

In all probability the first action taking place is the direct combination of oxygen in the same way as the combination of bromine or iodine, thereby forming a substance containing the group



, or the derived groups



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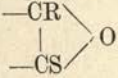

; this product then assimilating water whilst nascent.

Thus, for example, oleic acid, $C_{17}H_{33} . CO . OH$, may be supposed to combine with oxygen, forming $C_{17}H_{33}\begin{cases} = O \\ - CO . OH \end{cases}$. By taking up water this immediately produces dihydroxystearic acid, $C_{17}H_{33}\begin{cases} OH \\ OH \\ CO . OH \end{cases}$; whilst linolic acid, $C_{17}H_{31} . CO . OH$, similarly first forms $C_{17}H_{31}\begin{cases} = O \\ = O \\ - CO . OH \end{cases}$, which by taking up $2H_2O$ forms tetrahydroxystearic acid (sativic acid), $C_{17}H_{31}\begin{cases} OH \\ OH \\ OH \\ OH \\ CO . OH. \end{cases}$

In the case of the stearolic acid and its homologues obtained from acrylic acids by the bromine reaction (addition of Br_2 and removal of $2HBr$), the effect of oxidation stops short at the first stage, 2 atoms of oxygen being added on forming a saturated compound which does *not* take up water. Thus stearolic acid, $C_{17}H_{31} . CO . OH$, forms *stearoxylic acid*, $C_{17}H_{31}\begin{cases} = O \\ = O \\ - CO . OH \end{cases}$, melting at 84°-86° C., by the direct action of nitric acid (*Overbeck*),[2] or by means of alkaline permanganate (*Hazura* and *Grüssner*).

Similarly palmitolic acid (from hypogæic dibromide) gives the

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[1] *Ber.*, 1888, xxi., 1230 and 3343.

[2] Overbeck (*Annalen. Chem. Pharm.*, 1866, cxl., 39) found that the stearoxylic acid thus prepared would not combine with bromine, and concluded that the 4 affinity units which in stearolic acid were capable of combining with Br_4, were saturated by oxygen when stearolic acid was converted into stearoxylic acid.

analogous *palmitoxylic acid*, $C_{15}H_{27}\left\{\begin{array}{l}=O\\=O\\-CO\,.\,OH\end{array}\right.$, melting at 67° C. (*Schröder*); and benolic acid (from erucic dibromide) gives *benoxylic acid*,[1] melting at 90°-91° C., $C_{21}H_{39}\left\{\begin{array}{l}=O\\=O\\-CO\,.\,OH\end{array}\right.$ (*Haussknecht*).

By the action of heat (distillation in vacuo) dihydroxystearic acid (melting at 136° C.), loses water, and forms an anhydro derivative still possessing the characters of a monobasic acid (*Saytzeff*); obviously thus—

$$C_{17}H_{33}\left\{\begin{array}{l}OH\\OH\\CO\,.\,OH\end{array}\right. = H_2O + C_{17}H_{33}\left\{\begin{array}{l}=O\\ \\-CO\,.\,OH\end{array}\right.$$

the reaction being the converse of the second stage in the hydroxylation of unsaturated acids as above.

Natural Dihydroxystearic Acid.—According to *Juillard*[2] crude ricinoleic acid, when kept at a temperature below 12° C., deposits a crystalline substance. This consists of a mixture of dihydroxystearic and stearic acids, the latter of which can be removed by washing with hot toluene. On recrystallisation from boiling alcohol the dihydroxystearic acid melts at 141°-143° C. It is insoluble in ether, petroleum spirit, and benzene, but dissolves in boiling acetic acid and alcohol. When treated with reducing agents it is transformed into stearic acid. On being heated for some time at 220° C. in a current of carbon dioxide it is converted into a compound which is probably a polyhydroxystearic acid analogous to polyricinoleic acid.

When treated with hydrochloric acid at 180° C., and then saponified, it yields a dibasic acid—

$$COOH\,(HO)\,C_{17}H_{33}\,.\,O\,.\,C_{17}H_{33}\,(OH)\,COOH.$$

This melts at 50°-55° C.

About 1 per cent. of this dihydroxystearic acid can be obtained from castor oil.

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[1] Termed "dioxybenolic acid" by its discoverer.

[2] *Bull. Soc. Chim.*, 1895, xiii., 238.

§ 2. Physical Properties of Oils, Fats, Waxes, &c.

CHAPTER IV.

GENERAL PHYSICAL CHARACTERS.

PHYSICAL TEXTURE AND CONSISTENCY.

The physical consistency of a fixed oil—butter, fat, or wax—depends entirely upon the temperature; when this is sufficiently raised all are fluid oils; but at lower temperatures, according to the nature of the substance, more or less complete solidification is brought about. In many cases, natural fixed oils, etc., are mixtures of different glycerides, etc., the melting points of which are different; accordingly, at temperatures somewhat below the melting point of the least fusible constituent, this more or less completely solidifies, whilst the other constituents remain liquid, thus giving rise to pastiness or buttery texture. Substances of practically uniform composition (*i.e.*, consisting essentially of only one kind of compound) generally exhibit a fairly sharply defined melting point when the temperature is sufficiently raised; but this is not the case with mixtures; accordingly, considerably different temperatures will be registered as the melting points of such substances if different methods be employed, depending, for instance, in one case, upon the production of a considerable degree of softness only; in another, upon the complete liquefaction of all the constituents; and so on.

Even the most fluid oils possess to a greater or less extent the property of *viscosity*, or resistance to flow, due to the greater or less degree of cohesion between the constituent particles of the liquid. When the smooth surfaces of two solids are smeared or wetted with a viscous fluid and applied to one another, a varying degree of force will be requisite, according to circumstances, in order to enable one surface to glide over the other. The amount of force requisite in any given case largely depends on the viscosity of the fluid employed; to diminish this force is the main object of *lubrication* in the case of machinery, and in consequence the determination of the relative lubricating powers of different materials (lubricating oils, etc.) is an important point in the valuation for such purposes of different fixed oils, mixtures of these and mineral oils, and such like substances employed for the purpose. It is found that the rate at which a given fluid flows through an orifice of standard dimensions is in many cases a fair measure of its lubricating powers; whence the determination is frequently made of the rate of efflux of lubricating oils, etc., as compared with that of a standard fluid (such as rape oil), similarly examined in the same apparatus at the same temperature, the value deduced being generally (but by no means correctly) spoken of as the *relative viscosity* of the fluid examined (*vide* Chap. v.).

Cohesion Figures.

When a drop of oil is allowed to fall gently on the surface of water in a basin or large plate, it often behaves in a characteristic way, usually first spreading out into a thin film and then diminishing. It has been suggested that the particular forms assumed by films of various kinds (*cohesion figures*) are sufficiently well defined and characteristic to be of service in the examination of oils with a view to detecting adulteration; but any such method is hardly likely to give reliable results. Olive oil thus treated gives a fairly characteristic result, which is more or less modified by various admixtures, especially sesamé oil. Fig. 1 (*Schädler*) represents the different cohesion figures exhibited by colza oil (A, *Brassica rapa;* B, *Brassica napus*); poppyseed oil (C and D); sesamé oil (E); arachis oil (F); and olive oil (G).

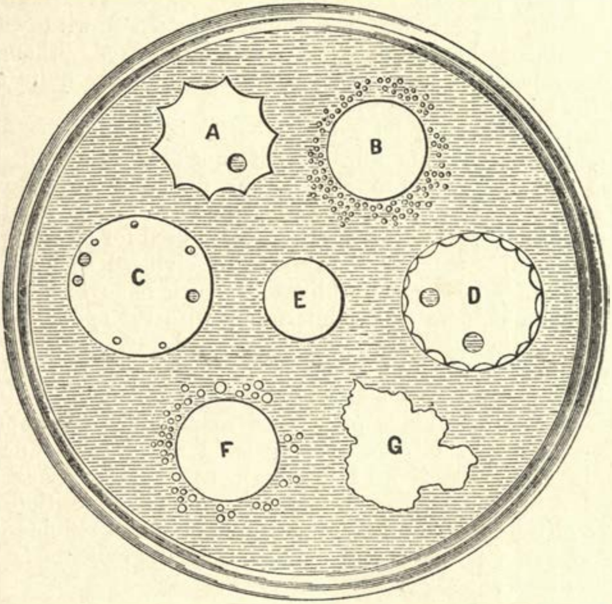

Fig. 1.—Cohesion Figures.

Taste and Odour.

When in a state of absolute purity, fixed oils have usually little or no odour or taste; but as met with in commerce, in most cases traces of sapid or odorous matters accompany the oil, so as to give a more or less characteristic flavour or smell thereto. Essential oils of the oxidised class, on the other hand, are frequently possessed of the most powerful scent, although the hydrocarbons which they contain, when completely separated from all traces of oxidised matter (by heating with sodium or other similar means), are generally odourless or practically so.

As regards the edible oils and fats, a considerable amount of their value depends on the delicacy and purity of the flavour; thus *genuine* olive oil is esteemed far more highly by connoisseurs than refined cotton-seed oil, arachis oil, and similar substances with which the ordinary commercial article is often largely intermixed, although, from the nutritive point of view, these latter are probably quite equal in value to the pure product of the olive.

Similarly, the commercial value of butter is largely affected by its flavour and freedom from all trace of rancidity or rankness; and analogous remarks apply to lard. The difficulty of removing all matters communicating unpleasant odour or taste to many varieties of fatty or oily matter often prevents these being used for dietetic purposes to any considerable extent, at any rate by civilised nations; in the case of some materials—*e.g.*, cod-liver oil—such removal is practically impossible without more or less interfering with the special characters and qualities of the substance.

Palm oil has generally a peculiar smell, recalling that of violets, and for certain purposes the possession of this odour is valuable—*e.g.*, in the preparation of certain kinds of scented soaps. The development of "rancidity" in fixed oils on keeping is in many cases due to the presence in small quantity of mucilaginous or albuminous matters which undergo chemical changes (oxidation, or decomposition, etc.) in the course of time; accordingly, the purification and refining of crude oils, etc., for the purpose of removing these ingredients is often a highly important operation.

Colour.

Expressed vegetable fixed oils sometimes possess a greenish shade, due to the presence of chlorophyll. As a general rule, cold-pressed oils of all kinds, prepared from fresh substances, are almost white; whilst oils subsequently expressed by the aid of heat, especially from materials that have been stored some time, are generally darker in tint, the hue varying from a light straw yellow to a light or even dark brown. Palm butter usually contains a dark orange-red colouring matter, different from chlorophyll; similar substances appear to be present in smaller quantity in many other oils, leading to the necessity for bleaching them for certain purposes. The refining processes, whereby mucilaginous extractive matters, etc., are removed, usually serve to lighten the colour also.

Spectroscopic Examination.

The addition of coloured vegetable expressed oils (containing chlorophyll, etc.) to animal oils, such as sperm oil may sometimes be detected by means of the absorption spectroscope [1] when such adulteration has been practised.

Olive oil shows three absorption bands (in the red, orange, and green), and sesamé oil gives a faint band in the red part of the spectrum. Castor and almond oils do not absorb any light. Refined cotton-seed oil shows absorption in the blue and violet, but its spectrum is continuous in the red and green parts of the spectrum.

Fluorescence.

This phenomenon does not appear to be exhibited by refined vegetable or animal oils free from substances possessed of fluorescent properties (such as æsculin, occasionally found in horse-chestnut oil); on the other hand, products of destructive distillation (coal-tar and rosin oils, etc.) often exhibit this peculiarity, so that admixtures of such hydrocarbons with more expensive vegetable and animal oils may sometimes be thus detected.

Action on Polarised Light.

The majority of the oils and fats in common use have so little action of a marked character on polarised light that little, if any, definite information of practical value is, as a rule, to be obtained by means of the polariscope. On the other hand, adulteration with strongly active hydrocarbons (such as some kinds of rosin oils) may sometimes be detected by a polarimetrical examination.

Bishop [2] obtained the (see p. 58) values for a length of 200 mm. of various oils in a Laurent polarimeter; the other figures annexed are from *Schädler*.

Peter [3] found most vegetable oils to be slightly lævo-rotatory, olive oil being an exception, so that admixtures of other oils may sometimes be detected by the rotation being left handed instead of right handed. Croton oil and castor oil, however, are comparatively powerfully dextro-rotatory, giving values exceeding + 40°.

The fatty acids, according to Peter, have the same rotatory power as the oils which contained them.

Rosin oil, which is a common adulterant of boiled linseed oil, has a dextro-rotatory power of 30°-50°. American turpentine is also

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[1] A special form of absorption spectrum colorimeter for this sort of examination has been devised by T. L. Paterson; *vide J. Soc. Chem. Ind.*, 1890, ix., 36.

[2] *J. Soc. Chem. Ind.*, 1887, vi., 750.

[3] *Bull. Soc. Chim.*, 1887, 483.

		Bishop.	Schädler.
		Degrees.	Degrees.
Lævo-rotatory,	Linseed oil, . . .	−0·3	−0·2
	Nut oil, ...	−0·3	...
	Apricot oil, . . .	...	−0·2
	Arachis oil, . . .	−0·4	−0·1
	Sweet almond oil, . .	−0·7	−0·2
	Colza oil, . . .	−1·6 to −2·1	−0·3
Neutral, or nearly so,	Cotton-seed oil, . .	...	0
	Poppy-seed oil, . .	0	+0·1
	Seal oil, ...	...	0
Dextro-rotatory,	Olive oil, . . .	+0·6	+0·2
	Cod-liver oil, . . .	...	+0·5 to +0·7
	Cold-pressed sesamé oil, .	+3·1	+1·0 to +1·1
	Hot ,, ,, .	+7·2	
	Castor oil, . . .	...	+9·8

dextro-rotatory, but the French turpentine rotates the beam to the left.

The Refractive Power.

The differences in refractive power exhibited by different oils are in some cases sufficiently marked to render this property of value in discriminating one from the other, or in detecting admixtures—*e.g.*, in the case of olive oil and cow's butter. Thus *Strohmer* gives the following values for the D line at 15° C., and *Abbé* the annexed values at 20° C., water being taken as 1·3330 :—

	Strohmer.	Abbé.
Olive oil, ...	1·4698 to 1·4703	1·4690
Almond oil, ...	...	1·4810
Sesamé oil (new), ...	1·4748	...
,, nine years old, . .	1·4762	...
Walnut oil, ...	...	1·491
Cotton-seed oil, ...	1·4732 to 1·4752	Crude, 1·4732 Refined, 1·4748
Rape and colza oil, ...	1·4720 to 1·4757	1·472 to 1·475
Beech-nut oil, ...	...	1·5000
Cold-drawn castor oil, . . .	1·4795	1·490
Hot-pressed ,, ...	1·4803	
Cold-drawn linseed oil, . . .	1·4835	1·4780
Poppy-seed oil, ...	1·4783	1·4670
Cod-liver oil, ...	1·4800 to 1·4852	1·4800
Whale oil, ...	...	1·483
Sperm oil, ...	...	1·470

From this it appears that olive oil has a considerably lower refractive index than the others, whilst drying oils and castor oil exhibit the highest values.

The following figures are due to *M'Ilhiney*[1]:—

	Refractive Index.
Linseed oil,	1·484 to 1·488 at 15° C.
Cotton-seed oil,	1·475 at 15° C.
Rosin oil,	1·535 to 1·549 at 18° C.
Mineral oil,	1·438 to 1·507
Rosin (colophony),	1·464 to 1 474
Maize oil,	1·478 at 20° C. 1·4765 at 15° C.
Fish oil,	1·480 at 15° C.

For the determination of the refractive power of oils and other substances *Abbé* and *Pulfrich* have devised special "refractometers."

Holde[2] obtained the following average results at 20° C. with Abbé's instrument :—

	Limits of Index of Refraction.	Mean Index.
Refined rape oil,	1·4722 to 1·4736	1·4735
Crude rape oil,	1·4735 ,, 1·4760	1·4744
Olive oil,	1·4670 ,, 1·4705	1·4698
Mineral oil,	1·4776 ,, 1·4980	1·4923
Rosin oil,	1·5274 ,, 1·5415	1·5344

The presence of rape oil in olive oil can thus be detected when any considerable amount of adulteration has been made.

The *Zeiss butyro-refractometer*, which is now extensively used, is shown in Fig. 2. This consists of prisms in casings, *A*, *B*, with a compensating arrangement for achromatising the critical line of total reflection of the standard substance for which the prisms are calculated, the special substance in this case being butter.

A few drops of the melted and filtered fat are allowed to fall upon the surface of the prism in *B*, which is then moved back to *A*, and secured by means of the pin, *F*. Meanwhile a current of water at the definite temperature is passed through *D*. The mirror, *J*, is then turned so as to show up the critical line separating the light and dark portions of the field, and the reading taken with the telescope.

A standard fluid is supplied with the instrument for the purpose of standardisation from time to time.

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[1] *Report on Linseed Oil*, 1901, 24.

[2] *J. Soc. Chem. Ind.*, 1891, x., 166.

The table on p. 59 shows the refractive indices corresponding to the degrees on the scale.

G. Marpmann,[1] in order to avoid the danger of injuring the apparatus by heating it to the point necessary to liquefy waxes or fats of high melting point, makes use of the fact that the refractive power of a mixture is the same as the sum of its constituents. Thus, equal parts of beeswax and peppermint oil gave a reading 47° in the butyro-refractometer at 40° C., and from this the refraction of the mixture was calculated to be $(2 + 47) - 50 = 44^\circ$. Clove oil and other ethereal oils were also found suitable solvents, but ether, chloroform, higher alcohols, benzene, etc., were less satisfactory.

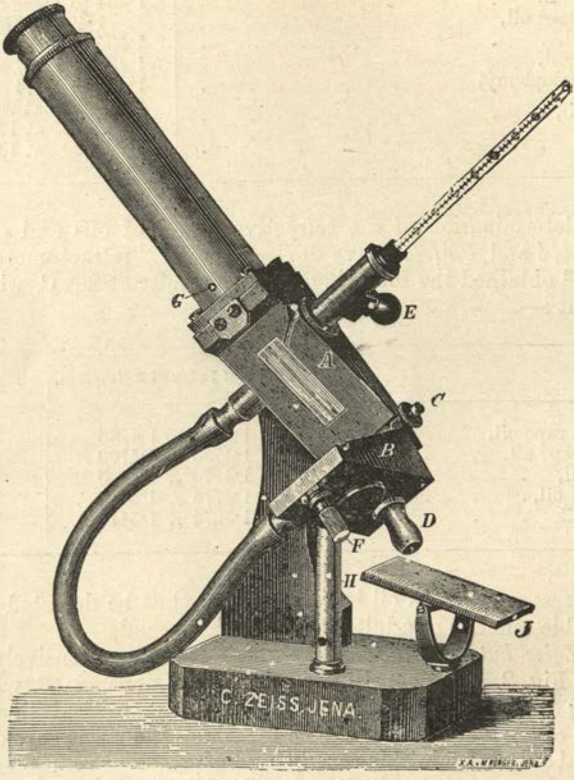

Fig. 2.—Zeiss Butyro-refractometer.

According to *Zeiss* the reading may be taken at any temperature, and then calculated to a standard temperature, say, 25° C. It has been shown by *J. Delaite*,[2] however, that this does not give concordant results with fats. He suggests that the standard temperature should be 40° C. for fats and 25° C. for oils.

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[1] *Chem. Rev. Fett Ind.*, 1901, viii., 65.

[2] *Bull. de l'Ass. belge. Chim.*, 1894, vii., 145.

Division on Scale.	n_D.	Difference.
0	1·4220	...
10	1·4300	8·0
20	1·4377	7·7
30	1·4452	7·5
40	1·4524	7·2
50	1·4593	6·9
60	1·4659	6·6
70	1·4723	6·4
80	1·4783	6·0
90	1·4840	5·7
100	1·4895	5·5

Specific Refractive Indices.—There exists a certain ratio between the specific gravity and the refractive index, though this is not absolute. Various formulæ have been proposed to obtain a refraction constant based upon the specific gravity and eliminating the effect of temperature.

In 1858 Gladstone and Dale proposed the empirical formula—

$$R_G = \frac{n-1}{d},$$

where R_G is the required constant, n the refractive index, and d the specific gravity.

A more recent formula is that of L. and H. Lorenz—

$$R_L = \frac{n^2-1}{(n^2+2)\,d}.$$

According to *Procter*[1] either formula gives good results in the special case of fats and oils, though the Lorenz value at different temperatures is, as a rule, the more constant. The Gladstone figures, multiplied by 0·6, give approximately the Lorenz values.

With the aid of the following table, abridged from that of Procter, the Lorenz constant is rapidly obtained by dividing the value corresponding to the observed refractive index (n) by the specific gravity.

For Calculating Lorenz Specific Refractions.

n.	$\frac{n^2-1}{n^2+2}$	Difference for $n = 0·01$.	n.	$\frac{n^2-1}{n^2+2}$	Difference for $n = 0·01$.
1·4000	0·24242	0·00534	1·450	0·26874	0·00515
1·4050	0·24510		1·455	0·27132	
1·4100	0·24776	0·00530	1·460	0·27389	0·00511
1·4150	0·25042		1·465	0·27645	
1·4200	0·25306	0·00526	1·470	0·27900	0·00508
1·4250	0·25570		1·475	0·28154	
1·430	0·25832	0·00523	1·480	0·28408	0·00504
1·435	0·26094		1·485	0·28661	
1·440	0·26355	0·00519	1·490	0·28912	...
1·445	0·26615				

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[1] *J. Soc. Chem. Ind.*, 1898, xvii., 1022.

Specific Refractions of Oils.

Oil.	Sp. Gr. at 15°C.	Refractive Index at 15°C.	Refractive Constants for 15°C.		Sp. Gr. at 60°C.	Refractive Index at 60°C.	Refractive Constants for 60°C.	
			$R_G = \frac{n-1}{d}$	$R_L = \frac{n^2-1}{d(n^2+2)}$			$R_G = \frac{n-1}{d}$	$R_L = \frac{n^2-1}{d(n^2+2)}$
Castor (average of 6), ...	0·963	1·4803	0·4987	0·2951	0·934	1·4647	0·4975	0·2958
Raw linseed (old), ...	0·935	1·484	0·5176	0·3060	0·8997	1·4674	0·5195	0·3086
,, (new), ...	0·930	1·481	0·5172	0·3060	0·9008	1·4657	0·5170	0·3073
,, (blown 48 hrs. at 100°C.),	0·9481	1·4862	0·5128	0·3029	0·9226	1·4698	0·5090	0·3023
Cod-liver (average of 3), . .	0·9359	1·482	0·5154	0·3049	0·9075	1·4659	0·5134	0·3051
Commercial cod, ...	0·9341	1·4831	0·5172	0·3058	...	...	...	...
Coast cod (average of 4), . .	0·9300	1·481	0·5172	0·3060	0·900	1·4635	0·515	0·3063
Whale (average of 4), . . .	0·9203	1·476	0·5162	0·3065	0·892	1·4603	0·5158	0·3072
Sardine (Jap.), ...	0·9256	1·479	0·5175	0·3063	...	...	...	...
Seal (pale), ...	0·9249	1·4784	0·5173	0·3063	0·8987	1·4619	0·5139	0·3059
Shark-liver, ...	0·917	1·4783	0·5216	0·3089	0·8918	1·462	0·518	0·3083
Cotton-seed, ...	0·9247	1·475	0·5137	0·3045	0·8943	1·4586	0·5127	0·3055
Earth-nut (4), ...	0·9212	1·4731	0·5136	0·3046	0·8899	1·4564	0·5128	0·3057
Maize (3), ...	0·9216	1·4765	0·5170	0·3063	0·8946	1·4605	0·5127	0·3065
Sesamé, ...	0·921	1·4746	0·5153	0·3057	0·8953	1·4580	0·5115	0·3048
Olive (4), ...	0·9166	1·4715	0·5144	0·3052	0·8903	1·4546	0·5106	0·3045
Rape (colza) (4), ...	0·9142	1·4745	0·519	0·3077	0·8854	1·4585	0·5201	0·3085
Neat's foot, ...	0·9163	1·473	0·5162	0·3062	0·8875	1·4559	0·5137	0·3062
Sperm, ...	0·882	1·4675	0·530	0·3149	0·8522	1·4508	0·529	0·3158
Mineral, ...	0·8654	1·4759	0·5499	0·3259	0·8383	1·4606	0·5494	0·3271

Procter has drawn up the results of his examination of a number of oils and fats in the subjoined tables, which show the refractive indices, specific gravities, and calculated Gladstone and Lorenz constants :—

Specific Refractions of Fats and Fatty Acids.

Substance.	Sp. Gr. at 60° C.	Refractive Index at 60° C.	Refractive Constants at 60° C.	
			$R_a = \frac{n-1}{d}$	$R_L = \frac{n^2-1}{(n^2+2)d}$
Fats.				
Wool fat (purified), . .	0·885	1·465	0·525	0·3124
Japan wax, . . .	0·907	1·450	0·495	0·2963
Oleostearine, . . .	0·907	1·449	0·495	0·2957
Palm-nut oil, . . .	0·896	1·443	0·495	0·2959
Butter fat (av. of 5), . .	0·897	1·4531	0·502	0·2998
Coconut oil, . . .	0·897	1·442	0·493	0·2950
Mutton tallow, . . .	0·9074	1·4531	0·499	0·2979
Beef fat, ...	0·901	1·442	0·490	0·2937
Buck tallow, . . .	...	1·4495	...	...
Horse fat, ...	0·894	1·455	0·509	0·3035
Bone fat, ...	0·894	1·451	0·504	0·3012
Lard, ...	0·886	1·452	0·510	0·3044
Palm oil, ...	0·8837	1·451	0·510	0·3047
Cacao butter, . . .	0·887	1·450	0·507	0·3030
Vaseline, ...	0·851	1·470	0·553	0·3070
Paraffin wax, . . .	0·776	1·434	0·559	0·3356
Fatty Acids.				
Stearic acid, . . .	0·8469	1·4361	0·5149	0·3088
Palmitic acid, . . .	0·851	1·434	0·510	0·3060
Oleic acid, ...	0·871	1·447	0·514	0·3072
Mixed tallow acids, . .	0·875	1·442	0·5051	0·3024
Mixed olive-oil acids (3), .	0·878	1·446	0·508	0·3037
Mixed cod-oil acids, . .	0·882	1·462	0·5238	0·3117
Möller's cod-oil acids, .	0·900	1·4645	0·5162	0·3069

The influence of the different elements on the specific refraction of a compound is best observed when calculated for unit weights as in the following table, quoted by *Proctor* from Conrady:—

Specific Refraction of Elements for Unit Weights.

Carbon (saturated), ...	0·1709
,, (ethylene), ...	0·3507
,, (acetylene), ...	0·3934
Hydrogen, ...	1·0510
Oxygen (hydroxyl), . . .	0·0951
,, (ethereal), . . .	0·1052
,, (carboxyl), . . .	0·1429
Chlorine, ...	0·1689
Bromine, ...	0·1116
Iodine, ...	0·1112

Hence it appears that the specific refraction is raised the most by hydrogen and the least by hydroxyl oxygen. This influence of oxygen is also shown in the next table, in which the hydroxystearic and ricinoleic acids show considerably lower values than oleic or stearic acids, whilst, on the other hand, the figure for paraffin (containing no oxygen) is much higher than that of the fatty acids containing the same number of carbon atoms.

The specific refraction of some of the principal fatty acids and glycerides, as calculated by *Procter* from Conrady's values, are :—

Substance.	Formula	Molecular Weight.	Specific Refraction, $\frac{n^2 - 1}{(n^2 + 2)d}$
Butyric acid,	$C_4H_8O_2$	88	0·2525
Tributyrin,	$C_3H_5(C_4H_7O_2)_3$	302	0·2526
Lauric acid,	$C_{12}H_{24}O_2$	200	0·2952
Trilaurin,	$C_3H_5(C_{12}H_{23}O_2)_3$	638	0·2927
Myristic acid,	$C_{14}H_{28}O_2$	228	0·2995
Trimyristin,	$C_3H_5(C_{14}H_{27}O_2)_3$	722	0·2970
Palmitic acid,	$C_{16}H_{32}O_2$	256	0·3026
Tripalmitin,	$C_3H_5(C_{16}H_{31}O_2)_3$	806	0·3002
Stearic acid,	$C_{18}H_{36}O_2$	284	0·3051
Tristearin,	$C_3H_5(C_{18}H_{35}O_2)_2$	890	0·3029
Arachidic acid,	$C_{20}H_{40}O_2$	312	0·3073
Triarachidin,	$C_3H_5(C_{20}H_{39}O_2)_3$	974	0·3051
Oleic acid,	$C_{18}H_{34}O_2$	282	0·3059
Triolein,	$C_3H_5(C_{18}H_{33}O_2)_3$	884	0·3036
Linolic acid,	$C_{18}H_{32}O_2$	280	0·3067
Trilinolin,	$C_3H_5(C_{18}H_{31}O_2)_3$	878	0·3043
Linolenic acid,	$C_{18}H_{30}O_2$	278	0·3075
Trilinolenin,	$C_3H_5(C_{18}H_{29}O_2)_3$	872	0·3055
Ricinoleic acid,	$C_{18}H_{34}O_3$	298	0·2946
Triricinolein,	$C_3H_5(C_{18}H_{33}O_3)_3$	932	0·2929
Hydroxystearic acid,	$C_{18}H_{35}(OH)O_2$	300	0·2939
Dihydroxystearic acid,	$C_{18}H_{34}(OH)_2O_2$	316	0·2854
Glycerol,	$C_3H_8O_3$	92	0·2225
Paraffin,	$C_{18}H_{38}$	254	0·3344

A high iodine value increases the constant, but this is not so apparent as in the refractive index, owing to the influence of an unsaturated structure on the specific gravity, as well as on the refraction.

An abnormally high specific refraction in an oil indicates the presence of hydrocarbons, or higher alcohols, such as wool fat and sperm oil. Low specific refraction may point to the presence of fatty acids of low molecular weight (as in the case of butter) or to hydroxylated or oxidised acids. The constant may thus be found to serve as a measure of the degree of oxidation that occurs in blown oils. A lower result would also be produced by the presence of halogens.

Oleorefractometer.—*Amagat* and *Jean*[1] have constructed an "oleorefractometer" (Fig. 3) whereby the refractive power of a given oil

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[1] *Comptes Rendus*, 1889, cix., 616 ; *J. Soc. Chem. Ind.*, 1890, ix., 113 and 218.

is determined by differential comparison with a sample of genuine oil taken as standard, a positive reading denoting increased refractive index and *vice versâ*. The following comparative differential values have been obtained by de Bruijn and von Leent and by Jean in this way, from which results they infer that the refractive powers of oils, when thus tested, are capable of giving more information as to admixture than is usually supposed. The oil to be examined should be previously shaken with alcohol to dissolve out free fatty acids; the standard of comparison is a sample of the purest olive oil obtainable; or, more commonly, a standard liquid supplied with the instrument.

It consists of a circular metal vessel, *t, t*, with two opposite lenses, *l, l*, in front of the glass sides, from which extend the two tubes, C L, the former of which ends in a collimator, V, and the latter in the telescope, O *c*. Within the centre vessel is an inner cell, C *y*, the glass sides of which form a prism; whilst in front of the telescope is placed an arbitrary photographic scale, E *c*, which measures the reading. A gas jet is used for the illumination, and the luminous field can be divided into a light and dark part by means of a slide.

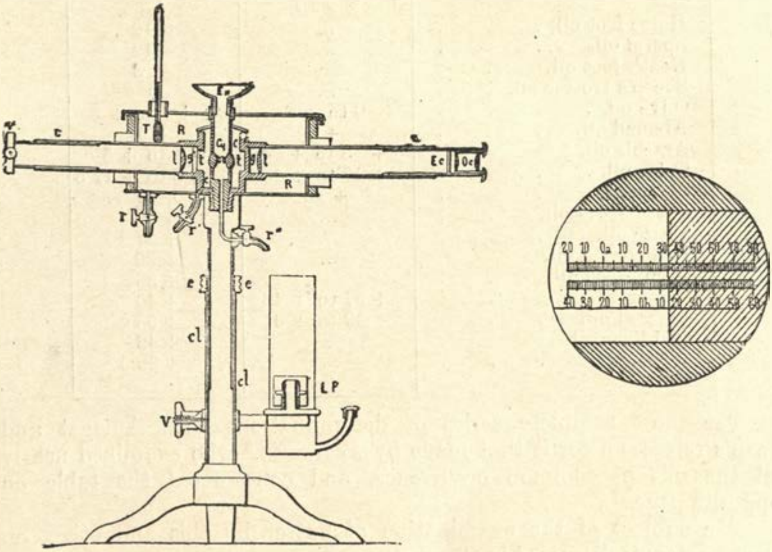

Fig. 3.—Oleo-refractometer.

If the inner cell and outer vessel contain the same liquid the shadow will fall upon the zero of the scale, but if they contain different liquids the shadow will fall to the left or right, according to the refractive power of the contents of the prismatic cell.

In making a determination the outer vessel is filled with an oil prepared by Jean, which gives a zero reading. The oil under examination is placed in the inner vessel, and an outer trough (not shown in the figure) filled with water. The whole of the contents are then brought to a temperature of 22° C., by means of the lamp, L P, and the reading taken.

Ellinger[1] uses solutions of different salts of known strength for the calibration of this instrument.

Bevan[2] suggests the use of a mixture of glycerol and water for standardising, in place of the special oil, which can only be obtained in Paris.

The subjoined results were obtained by *de Bruijn* and *v. Leent* and by *Jean* with this oleorefractometer :—

	de Bruijn and v. Leent.	Jean.
	Degrees.	Degrees.
Horse foot oil, . . .	...	− 12
Sperm oil, . . .	...	− 12
Neat's foot oil, . .	...	− 3
Sheep's trotter oil, . .	...	0
Olive oil, ...	0 to + 2	+ 1·5 to + 2
Almond oil, . . .	+ 7	+ 6
Arachis oil, . . .	+ 3 to + 4	+ 4 to + 5
Colza oil, ...	+ 15 to + 18	+ 16·5 to + 17·5
Sesamé oil, . . .	+ 45	+ 17
Cotton-seed oil, . .	...	+ 20
Maize oil, . . .	...	+ 27
Poppy-seed oil, . .	...	+ 30
Hemp-seed oil, . .	...	+ 33
Castor oil, . . .	+ 37 to + 46	+ 40
Linseed oil, . . .	+ 49 to + 54	+ 53
Cod-liver oil, . . .	...	+ 42
Whale oil, . . .	...	+ 30·5

The most complete series of determinations with Amagat and Jean's refractometer is that made by *Pearmain*,[3] who examined nearly all the oils of common occurrence, and constructed the table on opposite page.

The subject of the examination of butter by this and other refractometers is discussed in Chap. XIII.

Optical Dispersion of Oils.

In the case of certain oils, such as coconut and palm-kernel oils, the difference between optical dispersion is comparatively greater than the difference between the refractive indices.

The applicability of this character to the analysis of oils and fats has been studied by Fryer and Weston,[4] who used for the purpose a Zeiss-Pulfrich refractometer, and a hydrogen tube with a pressure of about 2 mm., the red and blue rays from which corresponded with

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[1] *J. prakt. Chem.*, xliv., 152 ; *Analyst*, 1891, xvi., 196.

[2] *Analyst*, 1895, xx., 135.

[3] *Analyst*, 1895, xx., 135.

[4] *Analyst*, 1918, xliii., 311.

Refractometer Readings of 244 Samples of Oils, etc.

Temperature, 22° C.	No. of Samples Examined.	Deviation.	Highest.	Lowest.	Average.
Almond,	8	+	10·5	8·0	9·5
Arachis (earth-nut),	5	+	7·0	5·0	6·0
Bottlenose,	1	+	50·0	50·0	50·0
Cabbage-seed,	1	+	15·0	15·0	15·0
Castor,	8	+	42·0	39·0	40·0
Cod-liver,	8	+	46·0	40·0	44·0
Cotton-seed (crude),	3	+	17·0	16·0	16·5
,, (refined),	6	+	23·0	17·0	21·5
Hemp-seed,	4	+	37·5	34·0	35·5
Japan-wood oil,	1	+	75·0	75·0	75·0
Lard oil,	6	−	1·0	0·0	0·0
Linseed (crude),	3	+	52·0	48·0	50·0
Linseed (refined),	5	+	54·0	50·0	50·0
Neat's-foot,	2	−	3·0	1·0	2·0
Niger-seed,	2	+	30·0	26·0	28·0
Olive,	105	+	3·5	1·0	2·0
Peach-kernel,	2	+	11·5	7·5	9·5
Pilchard,	2	+	36·0	32·0	34·0
Poppy-seed,	3	+	35·0	30·0	33·0
Rape,	8	+	20·0	16·0	17·5
Ravison,	2	+	24·0	20·0	22·0
Seal,	2	+	36·0	30·0	33·0
Sesamé,	5	+	17·0	13·0	15·5
Shark,	3	+	35·0	29·0	31·0
Sunflower,	1	+	35·0	35·0	35·0
Tallow oil,	2	−	5·0	1·0	3·0
Tea,	1	+	8·0	8·0	8·0
Whale,	2	+	48·0	42·0	45·0
Oleic acid,	3	−	33·0	29·0	32·0
Temperature, 45° C.					
Butter,	15	−	34·0	25·0	30·0
Margarine.	7	−	18·0	13·0	15·0
Lard,	10	−	14·0	8·0	10·5
Tallow,	6	−	18·0	15·0	16·0
Paraffin (soft),	2	+	58·5	54·0	56·0

the C and F lines of the spectrum. The readings were made at 40° C., and the refractive power was calculated by means of the formula—

$$\omega = \frac{n_F - n_C}{n_D - 1}.$$

It was found that most of the oils and fats examined showed very similar dispersions (0·0186-0·0207), with the exception of coconut oil (0·0167), linseed oil (0·0218), and tung oil (0·0371). Palm-kernel oil and butter fat also gave comparatively low figures (0·0180 and 0·0182 respectively), and the results indicate that the dispersion is lowered by the presence of glycerides of low molecular weight and increased by that of glycerides of highly unsaturated fatty acids. Each increase of 1° C. in the temperature reduces the dispersive power by about

0·00002. Free acidity has but little influence on the results, but heat-polymerisation causes a notable decrease in the value.

Heat of Combustion.

Sherman and *Snell*[1] have determined the heat of combustion of a large number of fats and oils, using an Attwater-Blakeslee bomb-calorimeter. The hydrothermal equivalent of the apparatus was determined by calculation from the weights and specific heats of the constituent material, and by combustions with pure cane sugar (= 3,959 cals. per gramme).

The results obtained were reduced to constant pressure by adding $(\frac{1}{2}p - q)\frac{M}{T}$ calories per gramme, where p represents the number of atoms of hydrogen; q, the number of atoms of oxygen in the molecule; M, the molecular weight of the substance; and T, the absolute temperature of the calorimeter.

The following corrections were required:—For American petroleum, 22 cals.; sperm oil, 18 cals.; castor oil and rosin oil, 14 cals.; and all oils consisting essentially of non-hydroxylated glycerides, 15 cals.

In making the combustion the oil was taken up with absorbent fibrous asbestos and ignited directly in the platinum crucible by means of an electrically fused iron wire.

The following table gives some of the chief results:—

Oil.	Specific Gravity at 15° C.	Iodine Value.	Free Acid as Oleic Acid.	Heat of Combustion, per Gramme.	
				Constant Volume.	Constant Pressure.
			Per cent.	Calories.	Calories.
Raw linseed (fresh), .	0·934	182·4	4·30	9364	9379
,, ,, (old), .	0·947	156·7	5·30	9215	9230
Boiled linseed, . .	0·953	150·7	7·40	8810	8824
Poppy-seed, . .	0·926	129·6	2·66	9382	9397
Maize, . . .	0·924	120·3	3·32	9413	9428
,, crude, . .	0·926	122·4	1·68	9419	9434
Cotton-seed (yellow), .	0·920	102·5	0·20	9396	9411
,, (old), .	0·941	93·7	2·03	9168	9183
Sesamé, . . .	0·924	105·3	1·65	9395	9410
Rape-seed, . . .	0·922	107·4	0·82	9489	9504
Castor, . . .	0·967	84·1	0·26	8863	8877
Arachis, . . .	0·917	105·9	0·16	9412	9427
Almond, . . .	0·919	98·1	5·13	9454	9469
Olive, ...	0·917	85·1	2·51	9457	9472
Menhaden, . . .	0·935	...	0·36	9360	9375
Cod-liver, . . .	0·927	165·6	0·56	9437	9452
Lard, ...	0·917	74·3	0·74	9451	9466
Sperm, . . .	0·886	78·7	0·78	9946	9964
Rosin, ...	0·989	76·9	14·40	10145	10159
Lubricating petroleum,	0·881	...	...	10797	10819

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[1] *J. Amer. Chem. Soc.*, 1901, xxiii., 164.

From these results Sherman and Snell conclude that castor oil, boiled linseed, and old oils have very low heats of combustion. The variations in the combustion heats stand in closer relationship to the specific gravity than to the iodine absorption or acidity. For oils of the same kind the product of the heat of combustion multiplied by the specific gravity is practically a constant unaffected by age or exposure. This constant is higher for drying than for non-drying oils. In the case of ordinary oils it was found to vary from 8·80 to 8·63. Castor and boiled linseed oils gave somewhat lower values, and sperm oil and mineral and rosin oils somewhat higher ones.

The heat of combustion divided by the specific gravity gave a result ranging from 10·0 to 10·3 for fresh unoxidised oils, 11·2 for sperm oil, and 11·8 to 12·3 for the mineral oils.

Schweinitz and *Emery*[1] give the following results obtained by *Attwater* with different solid fats :—Margarine, 9,599 to 9,795 ; butter, 9,320 to 9,362 ; oleo-margarine, 9,601 ; and lards, 9,503 to 9,654 calories per gramme. These figures for butter fat are higher than those obtained by *Stohmann*—viz., 9,192 calories by the potassium chlorate method and 9,231 calories by the oxygen method. Results obtained with mixtures of butter and margarine are also given.

Heat of Combustion of Fatty Acids.—The following values have been obtained by *Stohmann*, *Kleber*, *Langbein*, and *Offenhaur* :—[2]

Fatty acid.	Heat of Combustion.	Difference.
	Calories.	Calories.
Formic acid, CH_2O_2,	59·0	...
Acetic acid, $C_2H_4O_2$,	206·7	147·7
Propionic acid, $C_3H_6O_2$,	364·0	157·3
Normal butyric acid, $C_4H_8O_2$,	520·4	156·4
Normal valeric acid, $C_5H_{10}O_2$,	677·2	156·8
Isobutyl acetic acid, $C_6H_{12}O_2$,	832·2	155·0
Diethyl acetic acid, $C_6H_{12}O_2$,	832·3	155·1
Ethylpropyl acetic acid, $C_7H_{14}O_2$,	988·8	156·5
Dipropyl acetic acid, $C_8H_{16}O_2$,	1145·0	156·2
Heptyl acetic acid, $C_9H_{18}O_2$,	1302·3	157·3
Normal capric acid, $C_{10}H_{20}O_2$,	1458·3	156·0
Undecylic acid, $C_{11}H_{22}O_2$,	1615·9	157·6
Lauric acid, $C_{12}H_{24}O_2$,	1771·8	155·9
Myristic acid, $C_{14}H_{28}O_2$,	2085·9	157·0 × 2
Palmitic acid, $C_{16}H_{32}O_2$,	2398·4	156·2 × 2
Stearic acid, $C_{18}H_{36}O_2$,	2711·8	156·7 × 2
Arachidic acid, $C_{20}H_{40}O_2$,	3025·8	157·0 × 2
Behenic acid, $C_{22}H_{44}O_2$,	3338·3	156·3 × 2

Electrical Conductivity.

As yet but little use has been made of the difference in electrical conductivity of different fats and oils as a means of detecting adulteration. Generally speaking, this difference is not very marked, and

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[1] *J. Amer. Chem. Soc.*, 1896, xviii., 174.

[2] *J. prakt. Chem.*, 1894, xlix., 99.

hitherto the chief attempts have been made with the object of detecting the addition of other oils in olive oil, notably by *Palmiere*, who has constructed a special instrument or *Diagometer* for the purpose.

According to the experiments of *Herlant*[1] the electrical conductivity stands in direct relation to the refractive power and the critical temperature of solution. Salt solutions offer different resistance to an electric current, and the *specific resistance* of a solution is taken as the measurement for a cube with a side of 1 c.m., whilst the inverse function of this $\frac{1}{r}$ gives the *specific conductivity*.

To simplify the process, and to determine the *electrolytic capacity of the trough*, Herlant uses a salt solution of known conductivity on which to base his subsequent results. For this purpose he finds a $\frac{1}{500}$ N solution (1·49 grammes per litre) of potassium chloride satisfactory, the conductivity of this salt having been found by *Kohlenrausch* to be 0·002244 for a cubic centimetre at 18° C.

In the formula $\frac{1}{r} \times k = 0{\cdot}002244$, k represents the capacity of the trough, and when the potassium chloride solution is replaced by the solution to be examined the distance between the electrodes is modified, which gives the specific conductivity, l, of the solution

$$l = \frac{l}{r} \times k.$$

In the examination of fats and oils 10 grammes of the pure dry substance are saponified under a reflux condenser by means of 45 c.c. of pure normal alcohol potassium hydroxide solution, and the soap solution diluted to 250 c.c. and electrolysed.

The following results were thus obtained :—

Substance.	Butyro-refractometer (Zeiss) at 35° C.	Reichert-Meissl Value.	Critical Temperature of Solution.	Specific Conductivity at 18° C.
Butter, 1, . . .	44·5	28·7	98°-103°	0·006457
,, 2, . . .	45	28		0·00650
,, 3, . . .	45	28·6		0·006507
,, 4, . . .	48	25		0·00701
Margarine, 1, . .	52·5	3·2	122°-123°	0·008221
,, 2, . .	56·5	1·9		0·008459
,, 3, . .	54	2·0		0·008472
,, 4, . .	58	...		0·008489
Cotton-seed oil, . .	63	...	115°-116°	0·008629
Arachis oil, 1, . .	58·25	...		0·00870
,, 2, . .	60·25	...	123°	0·008741
Sesamé oil, . . .	63	...	120·5°	0·008779
Olive oil, . . .	57·25	...	123°	0·009927

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[1] *Bull. de l'Ass. belge Chim.*, 1896, x., 48.

After standing for a few weeks the soap solutions show a slight decrease in conductivity.

In Herlant's opinion the method may prove of service in the detection of margarine in butter, though in the case of oils the results are less promising.

Olive oil is usually stated to have a much lower conducting power than most other oils of ordinary occurrence, but it will be observed that in the results given above the soap solution from olive oil exceeds those of the other oils in the table as regards its conductivity.

SOLUBILITY OF OILS, FATS, ETC., IN VARIOUS SOLVENTS.

The immiscibility of "oil and water" is proverbial; but some few oils are known whose solubility in water is not inconsiderable. Thus the fusel oils of fermentation, and certain oxidised volatile essential oils, and products of distillation (*e.g.*, phenol), dissolve in water to the extent of a few per cents. by weight at ordinary temperatures.

As a general rule, however, fixed oils and hydrocarbons are, for practical purposes, entirely insoluble in pure water. In some few cases dilute alkaline solutions dissolve them somewhat more freely than pure water; in others the presence of acids slightly promotes solubility; but, as a rule, when neutral salts are present to any extent, their presence prevents the solution of the oil, etc.; so that on agitating an aqueous solution with solid common salt or with sodium sulphate, as the mineral matter goes into solution, the dissolved oil is more or less thrown out of solution. The same phenomenon is observed with the potassium and sodium salts of most of the fatty acids, so that when an aqueous solution of such salts (soaps) are treated with neutral saline matters, the organic salts are thrown out of solution; this property is largely utilised in the ordinary process of soap boiling.

Duyk[1] has shown that essential oils dissolve to a considerable extent in solutions of sodium salicylate, and has based a method of distinguishing between them on this property.

Strong alcohol does not exert any great degree of solvent action in the cold on most fixed oils, solid fats, or waxes; whereas, many essential oils, whether hydrocarbons or of oxidised nature, are readily dissolved. Similarly, resins and free fatty acids are, generally speaking, moderately soluble in alcohol, especially when the latter is almost anhydrous and warm. Some few fixed oils, too, are exceptional as regards solubility in alcohol, more especially *castor oil* and *croton oil*, and to a less extent coconut oil, cow's butter, and linseed oil.

Girard finds that absolute alcohol at 15° C. dissolves the following proportions of various oils :—

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[1] *J. Pharm. Chim.*, 1899, x., 448, 500.

Rape oil, Colza oil,	1·5-2·0 per cent.	Nut oil,	4·4 per cent.
		Beech-nut oil,	4·4 „
Mustard-seed oil,	2·7 „	Poppy-seed oil,	4·7 „
Hazel-nut oil,	3·3 „	Hemp-seed oil,	5·3 „
Olive oil,	3·6 „	Cotton-seed oil,	6·4 „
Almond oil,	3·9 „	Arachis oil,	6·6 „
Sesamé oil,	4·1 „	Linseed oil,	7·0 „
Apricot-kernel oil,	4·3 „	Cameline oil,	7·8 „

Schädler gives the following table representing the quantities of alcohol, of specific gravity 0·800, required to dissolve 1 part of oil or fat :—

	Cold.	Boiling.
	Parts.	Parts.
Almond oil,	60	15
Cacao butter,	...	4
Cotton-seed oil,	75	...
Croton oil,	36	...
Cameline oil,	68	...
Cod-liver oil,	45	6
Hemp oil,	30	Soluble in all proportions.
Japan wax,	...	3
Linseed oil,	40	5
Lard (hog's),	...	27
Madia oil,	30	6
Nut oil (walnut),	100	60 alcohol to 100 of oil.
Nutmeg oil,	...	4
Poppy-seed oil,	25	6
Tallow (sheep),	...	45
Suet (ox tallow),	...	40
Whale oil (bottlenose),	...	1

The Critical Temperature of Solution.

Crismer [1] applies this term to the point at which a substance brought into solution in alcohol under pressure just begins to separate out again. A few drops of the melted and filtered material are mixed with a slightly greater volume of alcohol of known density in a tube a few millimetres in diameter, which is subsequently sealed up and tied to the bulb of a thermometer by means of a platinum thread. It is then heated in a bath of sulphuric acid until the meniscus separating the two layers becomes a horizontal plane. At this point the tube is sharply turned two or three times so as to render the liquid homogeneous, after which it is replaced in the bath, the temperature of which is allowed to fall slowly, the thermometer and tube being meanwhile continually shaken. The temperature at which a perceptible turbidity appears in the tube is the critical temperature of solution.

Crismer plotted the curves obtained in the case of fats and hydrocarbons, and came to the conclusion that this constant was practically analogous to the *critical temperature* of the liquefaction of gases.

He also found that there was a sort of relationship between the

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[1] *Bull. de l'Ass. belge Chim.*, 1895-96, ix., 71, 143, and 359.

critical temperature and the amount of insoluble fatty acids in a fat, and that the critical temperature of solution of mixtures was approximately the arithmetical mean of those of its constituents.

He came to the conclusion that substances of the same nature had practically the same critical temperatures of solution. Thus. the following results were obtained with alcohol of 90 per cent. strength :—

Substance.	Critical Temperature of Solution.
	°C.
Butter, ...	99-106
Margarine, ...	122-125
Earth-nut oil, ...	123
Cotton-seed oil, ...	115·5
Sesamé oil, ...	120
Olive oil, ...	123
Almond oil, ...	120
Rape oil (crude), ...	136
,, (refined), ...	132·5
Hemp-seed oil, ...	97
Nut oil, ...	100·5
Blubber oil, ...	111·5
Castor oil, ...	0
Linseed oil (oxidised), ...	70
(With Alcohol of Specific Gravity 0·8195.)	
Mineral oils (various), ...	135·5-140
Valve oil, ...	197
Animal oil, ...	120
Sheep's foot oil, ...	102
Lard oil, ...	104
Neat's foot oil, ...	95
Colza oil, ...	132-135
Japan fish oil, ...	108

Asboth [1] gives the results of a number of tests which, in the main, confirm Crismer's results, but his figures were about 12° higher owing to his having used an alcohol of specific gravity 0·8332. Eight specimens of pure butter gave 111·5°-115°, while margarine showed 133° and 133·5°, and oleo margarine 142° C.

The following results were obtained by Stewart,[2] using a modification of the Crismer test, in which 3 c.c. of the filtered fat were heated with 3 c.c. of absolute alcohol in an open test-tube until clear, and the solution then stirred until the first signs of turbidity :—Butter fat, 50·5 to 57 ; margarine (from animal fat), over 65 ; (from vegetable fat) below 50 ; lard, 70 to 77 ; sesamé oil, 67·5 ; almond oil, 64 ; cotton-seed oil, 61·5 ; arachis oil, 57·5 ; olive oil, 56 ; cacao butter, 47 ; tallow, 34·5 ; palm oil, 22 ; coconut oil, 15 to 19·5 ; and palm-kernel oil, 13·5. Rape oil was insoluble in the boiling solvent.

The use of the critical temperature of solution in butter analysis is dealt with more fully in Chap. IX.

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[1] *Chem. Zeit.*, 1896, xx., 685.

[2] *J. State Med.*, 1918, xxvi., 312.

Solubility in Glacial Acetic Acid.

Valenta called attention to the suitability of glacial acetic acid as a means of separating certain oils from one another. Thus, *castor oil* and *rosin oil* will dissolve completely, even in the cold, whilst *rape oil, mustard-seed oil,* and *wild radish-seed oil* are not completely soluble even at the boiling point of the mixture.

Most other oils give a clear fluid while hot, which on cooling becomes turbid, owing to the smaller solubility of the oil in the acid at lower temperatures.

The Valenta Test.—*Valenta* [1] based a test for distinguishing between different oils by the different temperatures at which the turbidity is produced on cooling the hot solution, but this test has not met with general acceptance, mainly on account of the readiness with which the strength of the acid undergoes changes when exposed even for a short time to the air.

Thus the following figures, among others, have been recorded by *Allen*[2] and by *Hurst*[3] :—

Oil.	Valenta.	Allen.	Hurst.
	° C.	° C.	° C.
Olive (green),	85	...	28-76
,, (yellow),	111	...	
Almond,	110	...	...
Arachis,	112	87	72-92
Apricot-kernel,	114	...	...
Neat's foot,	...	102	65-85
Sesamé,	107	87	...
Melon-seed,	108	...	...
Cotton-seed,	110	90	53-63
Niger-seed,	...	49	...
Linseed,	...	57-74	36-41
Cod-liver,	101	79	65
Menhaden,	...	64	...
Shark liver,	...	105	95
Porpoise,	...	40	...
Sperm,	...	98	85
Bottlenose,	...	102	74-84
Whale,	...	38-86	48-71
Palm,	23	83	Not turbid at 13
Laurel-berry,	26-27	40	...
Nutmeg butter,	27	39	...
Coconut,	40	7·5	Not turbid at 13
Palm-kernel,	48	32	...
Bassia fat (Illipé),	64·5	...	...
Cacao butter,	105	...	...
Beef tallow,	95	...	...
Pressed tallow (m.p., 55·8°),	114	...	...
Tallow oil (cold pressed),	...	...	47
Hog's lard,	...	96·5	...
Lard oil,	...	...	69-76
Butter fat,	...	61·5	...
Oleomargarine,	...	96·5	...

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[1] *Dingler's Polytech. J.*, cclii.; *J. Chem. Soc.*, xlvi., 1078.

[2] *Commercial Organic Analysis*, 3rd ed., ii., [1], 41.

[3] *J. Soc. Chem. Ind.*, 1887, vi., 22.

Both *Allen* and *Hurst* came to the conclusion that the results were too variable and indefinite to be of service in discriminating the value of oils; and the same opinion was arrived at by *Ellwood*,[1] and by *Thomson* and *Ballantyne*,[2] the latter of whom obtained the following numbers, *inter alia*, with glacial acetic acid of different strengths:—

Name of Oil.	Percentage of Free Acid present (calculated as Oleic Acid).	Temperature of Turbidity with Glacial Acetic Acid of		
		Sp. Gr. 1054·2.	Sp. Gr. 1055·2.	Sp. Gr. 1056·2.
		° C.	° C.	° C.
Olive (Syrian),	23·88	42	...	...
,, (Gioja)	9·42	65	80	91
Same sample freed from free acid,	None.	87	...	...
Arachis oil (commercial),	6·20	76	96	112
,, (French refined),	·62	96	114	Not completely dissolved.
Rape oil,	4·54 2·43	105 110	Not completely dissolved.	,,
Linseed oil (Baltic),	3·74	42	59	71
,, (River Plate),	1·21	56	...	...
,, (East India),	·79	57	...	...

Chattaway, *Pearmain*, and *Moor*[3] introduced a more refined method of applying the test, and showed that by working under fixed conditions absolutely concordant results could be obtained. They found that it was necessary to observe the following points:—(1) Strength of acetic acid; (2) presence of water in the oil or fat; (3) the temperature to which the oil or fat had been previously heated; and (4) the method of stirring and observing the turbidity point.

In their method 2·75 grammes of the fat are mixed with exactly 3 c.c. of glacial acetic acid (99·50 per cent.) in a stoppered tube of about 4 ins. by ½ in. in size. This tube is heated in warm water, with continual shaking until a clear solution is obtained, after which it is placed in a beaker of warm water, with a thermometer attached to it, and allowed to rest until the contents change from clearness to turbidity.

They attribute the variations obtained by *Valenta* with different specimens of the same kind of oil (notably olive oil) to the presence of minute quantities of water having been overlooked. Moreover, when an oil had been unduly heated, they found that no reliance could be placed upon the turbidity figures.

The table at top of p. 76 gives results thus obtained.

E. Jones[4] emphasised the sensitiveness of the test to the smallest variations in the strength of the acetic acid. He found that the addition of only 0·2 per cent. of water lowered the turbidity temperature by 5°.

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[1] *Pharm. J.*, 3, xvii., 519.

[2] *J. Soc. Chem. Ind.*, 1891, x., 233.

[3] *Analyst*, 1894, xix., 147.

[4] *Analyst*, 1894, xix., 151.

Turbidity Temperatures with Acetic Acid (99·5 *per cent.*).

Oil or Fat.	° C	Oil or Fat.	° C.
Butter fat (24).		Seal (2),	65·0-70·0
Highest,	39·0	Japan fish oil (2),	47·5 and 19
Lowest,	29·0	Herring,	90·0
Mean,	36·0	Niger-seed,	68·5
Margarine (5).		Sunflower (2),	59-62·5
Highest,	97·0	Bottlenose (2),	80·0 and 96·0
Lowest,	94·0	Lard oil (3),	75·0-76·0
Mean,	95·5	Lard (4),	97·0-98·0
Olive oil (10),	83·0-91·0	Neat's foot oil,	72·0
Almond oil (5),	72-87	Tea oil,	78·0
Cotton-seed oil (7),	71-89·0	Rosin (2),	56·0
Cod oil (3),	26·5-31·0	Jamba oil (3),	Above 100
Cod-liver oil (3),	72·0-76	Cabbage oil,	,,
Colza (German),	83·0	Beef stearin,	,,
Rape oil (4),	63·0-78·0	Lard ,,	,,
Peach-kernel oil,	82·0	Castor oil,	Not above 18
Earth-nut (3),	72·0-73·5	Wool-grease olein,	,,
Linseed (3),	46·0-52·0		

In order to standardise his acid he used filtered butter fat of known turbidity temperature, and diluted each fresh lot of acid with water until it showed a turbidity at 60° C. with this particular butter, which was preserved in a stoppered bottle.

The following figures thus obtained with 3 c.c. of the fat in 3 c.c. of the acetic acid were obviously only relative, and depended upon the turbidity temperature of the standard fat :—

	° C.		° C.
Rape oil,	101	Lard oil,	96
Sesamé oil,	77	Cotton-seed oil,	76
Linseed oil (2),	53-57	Earth-nut oil (2),	61-88
Olive oil,	89	Butter fat,	40-70

The great objection to this method is that no two observers can be certain of working with acid of the same strength. Moreover, since butter fat rapidly changes on keeping, the standard itself cannot be relied upon for more than a short period.

In the present writer's opinion Valenta's test may give useful information when the precautions noted by *Chattaway*, *Pearmain*, and *Moor* are observed, but it should only be considered in conjunction with the results of other tests.

It is essential always to use acid of a fixed strength (preferably 99·5-99·8 per cent.) and continually to check the strength before making fresh tests. In titrating glacial acetic acid with alkali, however, it is practically impossible to be certain of the results within

0·2 per cent.—an error which makes a very great difference in the turbidity temperatures (*vide supra*). More accurate results can be obtained by checking the titration by the freezing point of the glacial acid, which varies considerably with the strength. Thus, *Rudorff* [1] gives the following corresponding figures :—

100 Parts of Mixture, containing	Solidifying Point.
	°C.
0·0 of water, . . .	+ 16·7
0·497 „ . . .	+ 16·65
0·99 „ . . .	+ 14·8
1·477 „ . . .	+ 14·0
1·961 „ . . .	+ 13·25

Mineral oils are but sparingly soluble in glacial acetic acid, so that on agitating with that solvent a mixture of mineral oil and other substances freely soluble in acetic acid, the latter are dissolved, leaving the former undissolved. In this way the presence of rosin oil is easily detected in paraffin and petroleum distillates.

Owing to the hygroscopic nature of acetic acid, *Fryer* and *Weston* [2] use as a solvent a mixture in equal volumes of 90 to 92 per cent. alcohol with amyl alcohol. This can be exposed to the air several hours without materially affecting the Valenta number. They suggest the use of pure almond oil with an iodine value below 100 for standardising the solvent, which is diluted so as to give a turbidity temperature of about 70° C. with this oil.

By means of this solvent it is possible to distinguish between animal and vegetable waxes (other than insect wax) and mineral waxes. For example, the following values were obtained :—Carnaúba wax, 82° ; candelilla wax, 63° ; beeswax, 76° ; spermaceti, 44° ; montan wax, 70° ; ozokerite, insoluble ; paraffin wax, insoluble ; and beeswax + 10 per cent. of ceresin, 82° C.

Heating an oil before applying the test has a great effect upon the ordinary Valenta results, but has only a slight influence on the amylethyl alcohol solvent.

To obviate the drawback of the solidification of the acetic acid in cold weather, *Parkes* [3] dilutes the acid with water and a lower fatty acid. A suitable solvent is prepared by adding 10 per cent. of butyric acid to glacial acetic acid and about 1 to 2 per cent. of water, to give the required turbidity temperature when standardised against pure butter fat.

Solubility in Other Solvents.

As a general rule, fixed oils are very freely soluble in *carbon bisulphide, chloroform, carbon tetrachloride, ether, benzene, light petroleum*

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[1] *Pharm. J.*, ii., 241.

[2] *Analyst*, 1918, xliii., 3

[3] *Analyst*, 1918, xliii., 82.

distillate (mostly consisting of pentane and hexane with their homologues), and *oil of turpentine;* and on this property are based various methods of extracting oleaginous matters from natural and other sources.

Castor oil, however, is almost insoluble in light petroleum spirit; whilst drying oils, when oxidised to some considerable extent, generally become either quite insoluble in these various solvents, or nearly so, the decrease in solubility usually being the more marked the greater the degree of oxidation. The action of nitrous acid on an oil (conversion into elaidin, Chap. VII.) usually diminishes the solubility of the oil.

MELTING AND SOLIDIFYING POINTS.

Thermometric Scales.—Of the different scales in use the Centigrade or Celsius scale is the one almost exclusively used for scientific purposes. In England, however, the highly inconvenient Fahrenheit scale is in common use for technical and general purposes; whilst in some parts of the Continent the Réaumur scale is similarly employed.

The following formula gives the means of translating the temperature expressed on any one of these systems into the corresponding value on either of the others, F being the value on Fahrenheit scale, C that on the Centrigrade scale, and R that on the Réaumur scale :—

$$\frac{F-32}{9}=\frac{C}{5}=\frac{R}{4}.$$

This formula is based on the system of construction of the three scales respectively; the distance between the "ice melting point" (sometimes termed the "freezing point") and the "steam point" (or "boiling point"—under normal atmospheric pressure) being divided into 180 degrees on the Fahrenheit scale, 100 on the Centigrade, and 80 on the Réaumur scale; so that the relative values of the degree in each scale respectively are—$\frac{1}{180} : \frac{1}{100} : \frac{1}{80}$; or $\frac{1}{9} : \frac{1}{5} : \frac{1}{4}$. The Réaumur and Centigrade scales, however, begin with the ice melting point as 0, so that the steam point is at 80° and 100° on the two scales respectively; whilst the Fahrenheit zero is 32° F. below the ice melting point; whence that point is 32°, and the steam point $32° + 180° = 212°$, on the Fahrenheit scale.

From the above formula the following equations are derived :—

$$C=\frac{5}{9}(F-32)=\frac{5}{4}R$$

$$F=\frac{9}{5}C+32=\frac{9}{4}R+32$$

$$R=\frac{4}{5}C \qquad =\frac{4}{9}(F-32).$$

The following table affords a yet simpler means of effecting the translation:—

Centigrade.	Réaumur.	Fahrenheit.	Centigrade.	Réaumur.	Fahrenheit.	Centigrade.	Réaumur.	Fahrenheit.
-40	-32	-40	+7	+5·6	+44·6	+54	+43·2	+129·2
-39	-31·2	-38·2	+8	+6·4	+46·4	+55	+44	+131
-38	-30·4	-36·4	+9	+7·2	+48·2	+56	+44·8	+132·8
-37	-29·6	-34·6	+10	+8	+50	+57	+45·6	+134·6
-36	-28·8	-32·8	+11	+8·8	+51·8	+58	+46·4	+136·4
-35	-28	-31	+12	+9·6	+53·6	+59	+47·2	+138·2
-34	-27·2	-29·2	+13	+10·4	+55·4	+60	+48	+140
-33	-26·4	-27·4	+14	+11·2	+57·2	+61	+48·8	+141·8
-32	-25·6	-25·6	+15	+12	+59	+62	+49·6	+143·6
-31	-24·8	-23·8	+16	+12·8	+60·8	+63	+50·4	+145·4
-30	-24	-22	+17	+13·6	+62·6	+64	+51·2	+147·2
-29	-23·2	-20·2	+18	+14·4	+64·4	+65	+52	+149
-28	-22·4	-18·4	+19	+15·2	+66·2	+66	+52·8	+150·8
-27	-21·6	-16·6	+20	+16	+68	+67	+53·6	+152·6
-26	-20·8	-14·8	+21	+16·8	+69·8	+68	+54·4	+154·4
-25	-20	-13	+22	+17·6	+71·6	+69	+55·2	+156·2
-24	-19·2	-11·2	+23	+18·4	+73·4	+70	+56	+158
-23	-18·4	-9·4	+24	+19·2	+75·2	+71	+56·8	+159·8
-22	-17·6	-7·6	+25	+20	+77	+72	+57·6	+161·6
-21	-16·8	-5·8	+26	+20·8	+78·8	+73	+58·4	+163·4
-20	-16	-4	+27	+21·6	+80·6	+74	+59·2	+165·2
-19	-15·2	-2·2	+28	+22·4	+82·4	+75	+60	+167
-18	-14·4	-0·4	+29	+23·2	+84·2	+76	+60·8	+168·8
-17	-13·6	+1·4	+30	+24	+86	+77	+61·6	+170·6
-16	-12·8	+3·2	+31	+24·8	+87·8	+78	+62·4	+172·4
-15	-12	+5	+32	+25·6	+89·6	+79	+63·2	+174·2
-14	-11·2	+6·8	+33	+26·4	+91·4	+80	+64	+176
-13	-10·4	+8·6	+34	+27·2	+93·2	+81	+64·8	+177·8
-12	-9·6	+10·4	+35	+28	+95	+82	+65·6	+179·6
-11	-8·8	+12·2	+36	+28·8	+96·8	+83	+66·4	+181·4
-10	-8	+14	+37	+29·6	+98·6	+84	+67·2	+183·2
-9	-7·2	+15·8	+38	+30·4	+100·4	+85	+68	+185
-8	-6·4	+17·6	+39	+31·2	+102·2	+86	+68·8	+186·8
-7	-5·6	+19·4	+40	+32	+104	+87	+69·6	+188·6
-6	-4·8	+21·2	+41	+32·8	+105·8	+88	+70·4	+190·4
-5	-4	+23	+42	+33·6	+107·6	+89	+71·2	+192·2
-4	-3·2	+24·8	+43	+34·4	+109·4	+90	+72	+194
-3	-2·4	+26·6	+44	+35·2	+111·2	+91	+72·8	+195·8
-2	-1·6	+28·4	+45	+36	+113	+92	+73·6	+197·6
-1	-0·8	+30·2	+46	+36·8	+114·8	+93	+74·4	+199·4
0	0	+32	+47	+37·6	+116·6	+94	+75·2	+201·2
+1	+0·8	+33·8	+48	+38·4	+118·4	+95	+76	+203
+2	+1·6	+35·6	+49	+39·2	+120·2	+96	+76·8	+204·8
+3	+2·4	+37·4	+50	+40	+122	+97	+77·6	+206·6
+4	+3·2	+39·2	+51	+40·8	+123·8	+98	+78·4	+208·4
+5	+4	+41	+52	+41·6	+125·6	+99	+79·2	+210·2
+6	+4·8	+42·8	+53	+42·4	+127·4	+100	+80	+212

Determination of Melting and Solidifying Points.

Inasmuch as most natural oils and fats, etc., are not chemically pure single substances, but generally consist of one or more main ingredients with smaller quantities of other allied bodies, as a general rule no sharply defined temperature exists characteristic of the melting or solidifying point of any given variety, although in many cases pure unadulterated specimens, even though of widely various origin do not differ largely in these respects. For the same reason, the point at which incipient solidification on chilling first becomes manifest, often differs considerably from the temperature at which the mass, when once rendered solid by cold, exhibits incipient fusion on gradual heating. Further, a given substance, if heated considerably above its melting point and then cooled quickly so as to solidify it again, will often melt for the second time at a temperature materially different from that at which it first fused, although the normal melting point is more or less regained on standing for some time; accordingly, if the fusing point of a solid fat that has been once melted is to be determined, a sufficient time must be allowed to elapse to enable the normal physical structure to be re-assumed (*vide infra*).

Fig. 4.—Capillary Tubes used for determining Fusing Points.

In practice, it is generally necessary first to melt the substance and then clarify it by subsidence, or, better, by filtration through dry paper, in order to remove suspended matters and, more particularly, water; so that the purified material, after cooling and solidification, must be allowed to stand some time (at least an hour or two, but preferably a much longer period, say till the next day) before further examination.

In order to determine the melting point of a solidified specimen, several different methods are in use, the results of which are not always comparable with one another; so that, if an accurate comparison of two substances is requisite, it is indispensable that *both must be examined by the same process, side by side.*

One of the most frequently used methods consists in preparing a capillary tube by drawing out in a flame a short piece of quill tubing (Fig. 4); the fine end is sealed up, and when cool, the solid to be examined is cut into very fine fragments or pulverised, and a little dropped in and shaken down into the capillary tube. This is then bound by wire, string, or an india-rubber ring to the stem of a thermometer (Fig. 5), so that the centre of the bulb is about level with the substance. The whole is then placed in a small vessel of water (or, for higher temperatures, melted paraffin wax) which is very slowly raised in temperature, either by means of a small flame underneath (Fig. 6), or, preferably, by placing it inside a much larger similar vessel; a large flask with the neck cut off and a small beaker answer well

(Fig. 7). *Olberg* employs for this purpose the circulatory arrangement shown in Fig. 8. This is filled with water or oil, the heat being applied at the base of A.

If circumstances permit, two such capillary tubes (or more) should be provided, one being used to obtain a first rough approximation to the melting point, and the others used subsequently to obtain a nearer result, the bath being previously slightly cooled below the first approximate value, and then very slowly heated again, so that several minutes are requisite to produce a rise in temperature of 2° or 3° C. The thermometer and attached tube are used as a stirrer during this heating, and the temperature noted when the fragments first show signs of melting. Frequently this temperature (*softening point*) is measureably below that requisite to cause the fragments to liquefy entirely, and run down to the bottom of the capillary tube as a clear fluid (*temperature of complete fusion*).

Fig. 5.—Mode of Attaching Tube to Thermometer.

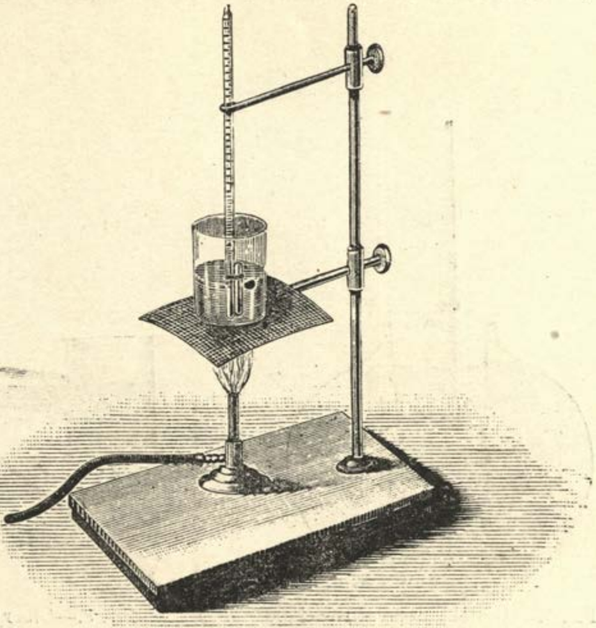

Fig. 6.—Method of Heating the Arrangement in Water.

Instead of a capillary tube sealed up at the end, one bent into a U or V shape may be employed, the solid particles being shaken down to the bend or angle. *Bennsemann*[1] modifies the tube by draw-

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[1] *J. Soc. Chem., Ind.*, 1885, iv., 535 ; from *Rep. anal. Chem.*, xi., 165.

ing it out as represented in Fig. 9. A drop or two of melted substance is introduced into the bulb portion of the tube, A, and fused as indicated by *a*. After standing for a sufficient time, the tube is placed in water, the temperature of which is very slowly raised; the temperature of incipient liquefaction is readily observed when the material softens and begins to run; at a little higher temperature it all runs down as indicated by *b*; when the turbid liquid becomes completely clear, the temperature of complete fusion is attained.

Another method of operating consists of drawing out the capillary tube as before, but *without* sealing up the narrow end. This end is then dipped into the melted substance to be examined and withdrawn. so that half an inch or so of the capillary tube is filled with the material. After standing at least an hour, but preferably till next day, the capillary tube is attached to the thermometer and placed in the bath as before. When the temperature rises to the softening point so as to produce incipient fusion, the plug of solid matter in the capillary tube becomes softened where it touches the glass, and is consequently forced upwards by the hydrostatic pressure of the fluid in the bath. When this occurs the temperature is noted.

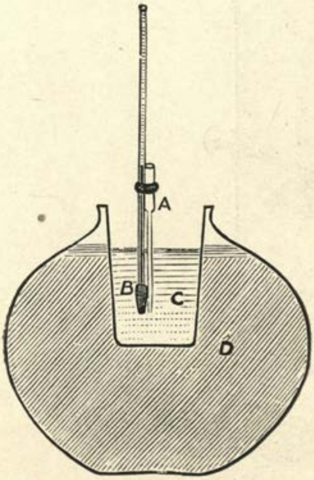

Fig. 7.—Another Mode of Heating in Water.

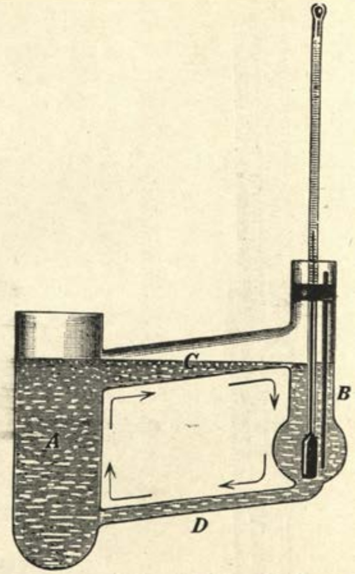

Fig. 8.—Olberg's Water Bath.

The former process is, as a rule, to be preferred, not only because it gives both the softening point and the temperature of complete liquefaction, but also, because by withdrawing the source of heat and allowing the completely fluid mass to cool slowly, the temperature at which re-solidification occurs can be more or less accurately determined.

With some kinds of mixed substances, the sealed-up capillary tube process enables three different temperatures to be ascertained, viz. :—Firstly, the temperature of incipient fusion when the most fusible constituent commences to melt; secondly, a temperature when this constituent has become so far melted that the solid fragments run down visibly; and thirdly, a still higher temperature *when the whole mass becomes clear and limpid*, showing that the whole of the less fusible constituents have also become completely melted. With certain mixtures of free fatty acids, etc., the difference between the lowest and highest fusion temperatures thus determined may amount to upwards of 5° C.

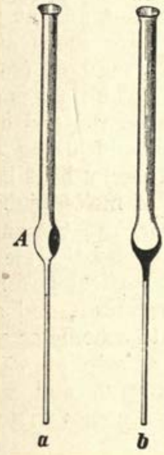

Fig. 9.—Bennsemann Tubes.

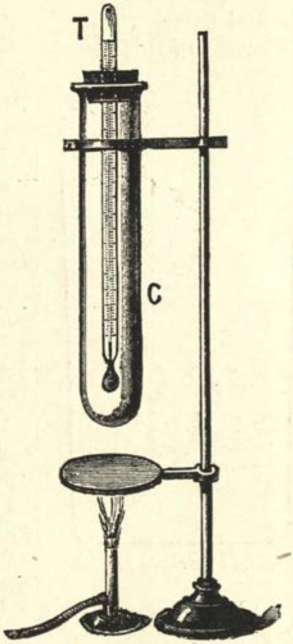

Fig. 10.—Pohl's Method.

Softening Point.—A convenient method of determining the softening point in certain cases consists in dipping the bulb of the thermometer into the melted material to be examined, and causing a small light glass bulb or float to adhere to the thermometer, cemented thereto by the substance as it solidifies. After waiting a sufficient time to enable the mass to attain its normal physical structure, the thermometer and bulb are placed in a bath, which is gradually heated.

When the temperature attains the softening point, the float becomes detached and rises up in the fluid.

Instead of a float, a thick coating of the substance itself may be applied to the thermometer by dipping the latter in the just-melted substance for an instant, taking out again until the adherent film has solidified, and repeating the operation two or three times so as finally to obtain a sufficiently thick coating. Fig. 10 represents Pohl's form of bath for the purpose, consisting of a wide test-tube, C, through the cork in the mouth of which passes the thermometer, T, the heat being applied by means of a small flame impinging on a flat metal disc, supported a little distance below the test-tube, so as to furnish an ascending current of warm air. Obviously a vessel of warm water may be substituted for the disc and flame.

A modification of this plan has been suggested by *Cross* and *Bevan*,[1] in which a thin piece of sheet iron (ferrotype plate) is cut into the shape shown in Fig. 11, about ¾ inch long and ⅜ or ½ inch across. At A the plate is hammered so as to form a minute saucer or depression, and at B a hole is cut of such size as to allow the plate to fit on to the bulb (conical) of a thermometer. The float is made by blowing a bulb on the end of a thin piece of tubing, and fixing a bit of platinum wire therein, bent into an L shape. A drop of melted substance is put in the saucer, and the end of the wire dipped into it, the stem being supported in a vertical position until the substance solidifies, and so holds it firmly. The thermometer and float are placed in a bath of water, etc. (preferably mercury), and when the temperature rises to the softening point, the float becomes detached and rises to the surface.

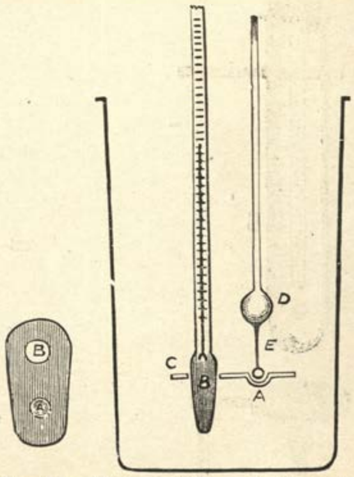

Fig. 11.—Cross and Bevan's Method

To obtain concordant results by the thermometer bulb methods it is essential that identical conditions should be observed. *Meldrum*[2] has also found that sufficient fat should be attached to the bulb to form two drops. In the case of very soft products a convenient method is to cool the bulb below 0° C. and then to dip it rapidly into the material.

In many cases the temperatures of incipient fusion and of complete liquefaction may be easily determined by placing small fragments or pinches of powder of the substance examined on the surface of a bowl of perfectly clean mercury, in which is placed a thermometer, and gradually raising the temperature. When complete fusion is

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[1] *J. Chem. Soc.*, 1882, xli., 111.

[2] *Chem. News*, 1913, cviii., 233.

effected, the substance becomes a minute drop of clear fluid, which usually spreads out film-wise over the surface of the mercury.

An ingenious modification of this method has been proposed by *J. Loewe*,[1] on which the substance is first applied to the end of a platinum wire (by dipping into the just-fused substance), so as to cover it completely. The coated wire is then supported by means of an insulating holder of glass, just below the surface of the mercury, and connected with one pole of a small galvanic cell, whilst the mercury is connected with the other pole. So long as the substance is unmelted no contact takes place between the platinum wire and mercury; but as soon as fusion takes place contact is brought about, and an electric bell included in the circuit is made to ring. Fig. 12 represents the general arrangement employed, the mercury being placed in a capsule heated over a small water-bath, the temperature of which is ascertained by means of a thermometer.

Instead of a platinum wire coated with the substance examined, *Christomanos*[2] employs a drawn-out capillary tube into which the melted substance is introduced, a platinum wire being imbedded in the material. After solidifying and standing sufficiently long to attain the normal texture of the substance examined, the capillary tube is heated in a mercury bath, electrical connections being applied to the bath and platinum wire, so that when the substance fuses, contact is made and a bell rung.

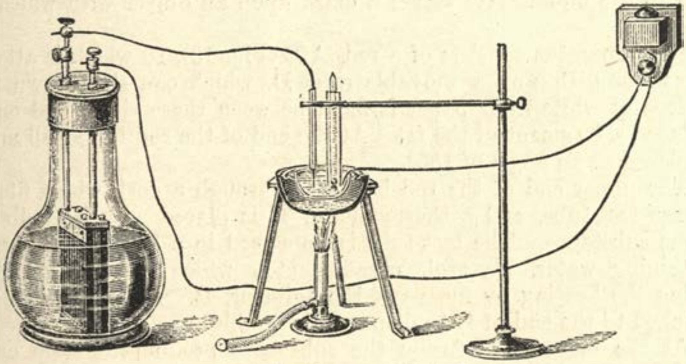

Fig. 12.—Loewe's Method.

A similar arrangement is in use in the Paris Municipal Laboratory, the substance tested being placed in the bend of a U-shaped tube with a platinum wire in each limb, together with some mercury, which runs down and makes contact when fusion occurs.

Le Sueur and Crossley's Method.[3]—This is based upon the capillarity of liquid substances, and has the advantage of eliminating the

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[1] *Dingler's Polytech. J.*, cci., 250.

[2] *Ber.*, 1890, 1093; *J. Soc. Chem. Ind.*, 1890, ix., 891.

[3] *J. Soc. Chem. Ind.*, 1898, xvii., 988.

previous melting of the substance so as to introduce it into the tube. A small portion of the material is placed in a tube about 75 mm. in length by 7 mm. in diameter, and a fine capillary tube, open at both ends and not exceeding 0·75 mm. in diameter, is introduced so that one end is well surrounded by the substance. The whole is attached to a thermometer and immersed in a beaker of water which is slowly heated with continual stirring until the substance is seen to rise in the capillary tube. The temperature at which this occurs is taken as the melting point. In certain cases the fat is only completely melted within a wide range of temperature, and consequently this method only shows the melting point of that portion first completely liquefied. *Le Sueur* and *Crossley*, however, recommend that even in such cases this temperature should be taken as the melting point. With ordinary fats duplicate results agree within 0·2° C.

Vandevyver's Method.—*Vandevyver*[1] takes as the melting point of a substance the temperature at which a substance in passing from the solid to the liquid state leaves a mark upon an object with which it is in contact.

His apparatus consists of a rod, A B (Fig. 13), to which is attached a fixed ring, C, and a movable ring, D, which can slide down to C. A piece of white filter paper is fixed between these rings, and on this is placed a fragment of the fat. At the end of the rod is a small mirror, M, placed at an angle of 135°.

The upper end of the rod is passed through a cork which fits into a large test-tube, and a thermometer, T, is placed with its bulb close to the substance. The test-tube is immersed in a beaker, V (Fig. 14), containing water, glycerol, paraffin, etc., which is kept in motion during the heating by means of the agitator, R. A small brush, S, is attached to the end of R to disperse air bubbles.

At the moment of fusion the substance produces a stain on the filter paper, which is reflected by the mirror. A piece of ground or polished glass can be substituted for the paper when the substance produces a stain in the solid condition.

Solidification Point of Oils.—If the melting point of a fluid oil that has been solidified by chilling is to be determined, the bath used must be itself cooled down below the melting point, and gradually allowed to rise in temperature. Strong brine, glycerol diluted with a little water, or calcium chloride solution may be conveniently used for temperatures below 0°.

When the solidification point of a fluid oil or melted fat is to be determined, a rough approximation may often be obtained by placing some in a small narrow test-tube, or dipping into the fluid a loop of platinum wire so as to cause a small drop to adhere, and immersing in a bath of water, brine, etc., which is being cooled down by an external application of broken ice or snow and salt, or ether through which air is blown, etc., noting the temperatures when transparency first ceases, and when visible solidification of the whole mass has ensued.

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[1] *Ann. de Chim. Anal.*, 1898, iii., 397.

Superfusion.—In most cases, however, the temperatures thus ascertained are too low, because superfusion is extremely apt to occur with oils and fats. If, however, a moderately large quantity of substance be used (15 to 20 grammes at least), it frequently occurs that, as soon as solidification begins, a more or less considerable rise in temperature of the mass takes place, just as when water cooled down below 0° in a dustless still atmosphere rises to 0° whenever freezing actually commences; or just as the temperature of a supersaturated solution of Glauber's salt (sodium sulphate) rises when the fluid sets to a crystalline mass. The higher temperature thus indicated is permanent for a time as solidification goes on, and is usually much more nearly exact than the lower one attained before solidification commenced; but even this higher one is often several degrees below the temperature of incipient fusion (and *a fortiori* below that of complete fusion) indicated when the mass has been solidified completely, allowed to stand some time, and then re-melted in a sealed-up capillary tube.

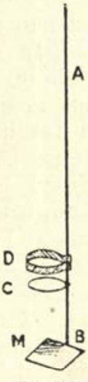

Fig. 13. Vandevyver's Method.

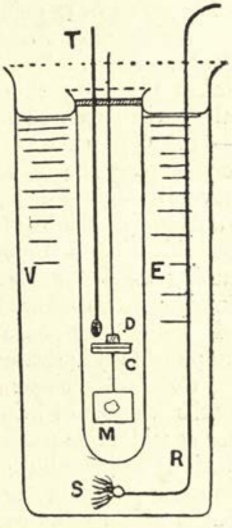

Fig. 14.—Vandevyver's Apparatus.

Differences of this description are more usually observed when the substances in question are mixtures of different constituents melting at different temperatures; on the other hand, a single substance in a state of moderate purity (*e.g.*, a well purified sample of a given fatty acid, such as stearic acid) usually shows but little difference between the temperatures of incipient fusion and of complete fusion in a closed capillary tube, and those where the limpid fused mass first shows signs of turbidity, and where visible complete solidification occurs, on slightly cooling the melted substance.

Phenomenon of Double Melting Point.—As was mentioned above, certain fatty substances appear to undergo a physical change after being melted, so that when again solidified they have a different melting point than before. This is notably the case with the mixed glyceride isolated by *Heise*[1] from mkani fat. This oleo-distearin as first obtained by *Henriques* and *Kunne*[2] by crystallisation from ether and alcohol melted at 44·5° to 45·5° C., but, having once been melted, its melting point was 38·5° to 39·5° C.

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[1] *Arbeit. a. d. kaiserl. Gesundheitsamt*, 1896, 540.

[2] *Ber.*, 1899, xxxii., 387.

Heise[1] recorded a third melting point in the same substance, for on melting it and cooling it rapidly until solid, he showed that it would re-melt at 27° C., and that if the heat were applied more slowly the formation of crystals could be observed, which did not melt until 37° to 38° C. He attributed the phenomenon to the production of allotropic modifications similar to those which are known in the case of sulphur.

Analogous phenomena of double melting points have been observed by *Albitzky*[2] in the case of chlorostearic acid, by *Holde* and *Stange*[3] in the case of mixed glycerides isolated by them from olive oil, and by *Bömer*[4] in that of the mixed glycerides from lard and beef fat.

The true explanation of this phenomenon has been given by *Grün* and *Schacht*,[5] who found that in such cases two isomeric modifications of the glycerides were present, each of which had a different melting point, and that there was a gradual transformation of the modification of lower melting point into that of higher melting point.

Influence of Time.—With some kinds of oils, *time* is an important factor in the determination of the temperature at which solidification takes place on chilling, inasmuch as frequently no solidification at all is visible on cooling for a short time to a given temperature (*e.g.*, — 15° C.), whereas more or less complete solidification takes place on keeping the oil for several hours at a temperature not so low by several degrees (*e.g.*, — 5°). In most cases, if a fragment of oil, previously solidified by chilling, be dropped into cooled oil, solidification is brought about much sooner, the particle introduced acting as a " nucleus " and facilitating crystallisation in the well-known way observed with other bodies (*e.g*, supersaturated solution of sodium sulphate; superused metals; glycerol; monohydrated sulphuric acid; water chilled down whilst at rest below 0°, etc.).

Constant Temperature Baths.—For determinations of this kind, baths capable of being maintained at fairly constant low temperatures for considerable periods are requisite. Hoffmeister uses for this purpose various saline solutions cooled externally by a freezing mixture; by suitable choosing the saline substance and the strength of its solution, baths of constant temperature can be obtained so long as any liquid remains unsolidified or any solid unmelted. Thus the following temperatures correspond with solutions of the respective strengths :—

Temperature.	Solution.	
° C.		
0	Distilled Water.	
— 2·85 to — 3·0	Potassium nitrate, .	13 parts per 100 of water.
— 5·0	Potassium nitrate, .	13 ,, ,,
	Sodium chloride, .	3·3 ,, ,,
— 8·7 to — 9·0	Barium chloride, .	35·8 ,, ,,
— 15·4 to — 15·0	Ammonium chloride,	25 ,, ,,

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[1] *Chem. Rev. Fett Ind.*, 1899, vi., 91.

[2] *J. prakt. Chem.*, 1900, lxi., 94.

[3] *Ber.*, 1901, xxxiv., 2402.

[4] *Zeitsch. Nahr. Genussm.*, 1913, xxv., 321.

[5] *Ber.*, 1907, xl., 1778.

Chilling baths of this description are more especially of use in determining the congealing point of lubricating oils.

Recorded Melting and Solidifying Points.—The following table, derived in the main from Schädler's *Technologie der Fette und Oele*, shows the average melting and solidifying points of many of the more commonly occurring fats and oils :—

Solidifying and Melting Points of Oils, etc.

Name.	Melting Point after Solidification.	Solidifying Point when Cooled (after Fusion, if Solid).
	° C.	° C.
Arachis (earth-nut) oil,	..	− 3 to − 4
Almond oil,	..	− 20
Bassia fat (Galam butter),	28 to 29	21 to 22
Beech-nut oil,	..	− 16·5 to − 17·5
Belladonna-seed oil,	..	− 16
Ben oil,	..	About 0
Bone grease,	44 to 45	35
Butter,	29 to 35	28 to 30
Cacao butter,	33 to 34	20·5
Castor oil,	..	− 18
Coconut oil,	24·5	20 to 20·5
Colza oil,	..	− 6
Cotton-seed oil,	..	− 2
Cress-seed oil,	..	− 15
Croton oil,	..	− 16
Goa butter (*Brindonia indica*),	40	32
Goose grease,	26	18
Grape-seed oil,	..	− 16
Gourd-seed oil,	..	− 15
Hazel-nut oil,	..	− 17 to − 18
Hemp-seed oil,	..	− 27 to − 28
Japan wax,	53 to 54	40 to 41
Laurel-berry fat,	38	30
Linseed oil,	..	− 19
Madia oil,	..	− 15
Nut oil,	..	− 28
Nutmeg butter,	43·5 to 44	33
Oleic acid,	..	− 6
Olive oil,	..	2 to 4
Poppy oil,	..	− 16 to − 18
Palm oil,	30 to 41	21 to 37
Pine oil,	..	− 18
Rape-seed oil (*Brassica napus oleifera*),	..	− 3
Radish-seed oil,	..	− 4
Sesamé oil,	..	− 5
Spindel oil (*Euonymus europæus*),	..	− 10
Sunflower-seed oil,	..	− 16
Tallow,	46 to 50	36 to 40
Tobacco oil,	..	− 25
Train oil,	..	0 to − 2
Virola fat (*Virola sebifera*),	45	40
Wax,	62 to 64	About 60
Whale oil,	..	0 to − 2

Wimmel.

	Melts at	Becomes Turbid at	Temperature rises during Solidification to
	° C.	° C.	° C.
Sheep's tallow (fresh), . .	47	36	40 to 41
,, (old), . .	50·5	39·5	44 to 45
Ox tallow (fresh), . .	43	33	36 to 37
,, (old), . .	42·5	34	38
Hog's lard, ...	41·5 to 42	30	32
Butter (fresh), . . .	31 to 31·5	19 to 20	19·5 to 20·5
Cacao butter, . . .	34 to 35·5	20·5	27 to 29·5
Coconut oil, . . .	24·5	20 to 20·5	22 to 23
Palm butter (fresh), . .	30 to 36	21 to 24	21·5 to 35
,, (old), . .	42	38	39·5
Nutmeg butter, . . .	43·5 to 44	33	41·5 to 42
Beeswax, ...	62 to 62·5	...	...
Spermaceti, ...	44 to 44·5	...	...

Rudorff.

	Melts at	Solidifies at
	° C.	° C.
Yellow wax, ...	63·4	61·5 to 62·6
White wax, ...	61·8	61·6
Spermaceti, ...	43·5 to 44·3	43·4 to 44·2
Japan wax, ...	50·4 to 51	...
Cacao butter, ...	33·5	...
Nutmeg butter, ...	70 to 80	...
Sheep's tallow, ...	46·5 to 47·4	32 to 36
Ox tallow, ...	43·5 to 45·0	27 to 35

Effect of Hydrolysis.—The melting point of a pure glyceride, or mixture of glycerides, is often materially altered if, as is often the case, any considerable amount of hydrolysis has taken place, either through development of "rancidity" through fermentative changes taking place on account of the presence of mucilaginous or albuminous matters, or by the agency of acids during refining, or otherwise. Hence, the numbers obtained with various samples of otherwise pure oils (*i.e.*, unadulterated with cheaper ones) are apt to vary.

Fatty Acids.—More nearly concordant figures are obtained if the whole of the glyceride is saponified by means of alkalis (*e.g.*, alcoholic potassium hydroxide), and the fatty acids separated from the resulting soap by evaporating off alcohol, dissolving the residue in hot water, acidulating with a mineral acid in excess, thoroughly agitating till all the soap is decomposed, and finally allowing the liquid to cool, and removing the cake of solidified fatty acids that separates out on standing.

By determining the melting point of the fatty acid cake thus produced side by side with that similarly prepared from a sample of oil of known purity, or from a mixture of known character, useful indications as to purity or otherwise can often be obtained. For example, the fatty acids from genuine olive oil usually melt at from 22° to 26° C., and those from refined cotton-seed oil at 35° to 40° C., so that any considerable admixture of cotton-seed oil with olive oil will usually result in yielding a cake of appreciably raised melting point. The amount of rise, however, does not give any very clear indication of the amount of admixture, because, as a general rule, mixtures of different substances melt at a temperature lower than that calculated arithmetically from the relative amounts and melting points of the ingredients (see *Heinz's* tables, *infra*).

Recorded Melting and Solidifying Points of Fatty Acids.—The following table represents the melting and solidifying points of the mixed fatty acids obtained from various oils and fats, as given by *Schädler* :—

Name of Oil, &c.	Melting Point.	Solidifying Point.
	°C.	°C.
Apricot-kernel,	4·5	0
Almond,	14	5
Arachis,	32 to 33	29 to 30
Butter,	37	33
Cacao butter,	49·5	46·5 to 47
Castor,	13	3
Charlock,	18 to 19	13
Chinese tallow,	57	52
Cotton-seed,	37 to 38	32·5
Coconut,	24 to 25	20 to 20·5
Colza,	20 to 21	14 to 14·5
Galam butter,	35·5	30
Hemp,	19	15
Lard,	38 to 39	35
Linseed,	17	13·5
Lallemantia,	11 to 12	...
Malabar tallow,	56·5	54·8
Margarine,	42	39·4
Nutmeg,	42·5	40
Nut (walnut),	20	16
Olive,	26·5 to 28	21·5 to 22
Poppy,	20·5	16·5
Palm,	45 to 46	42 to 43
Rape,	21	16
Suet (ox),	45·5	43
Sesamé,	35 to 36	31·5 to 32
Spermaceti,	13·5	...
Sunflower,	23	17
Tacamahac,	36·5	31
Tallow (sheep),	49	45
Ungnadia,	19	10
Wool grease,	41·8	40

Slightly different values have been given by other observers, the variations arising partly from differences between the particular specimens examined and partly from differences in the mode of observation. Thus, the figures below given by *Hübl* are respectively the temperatures of complete liquefaction (as obtained by melting in a narrow test-tube, stirring with a thermometer, and noting the temperature when turbidity disappeared), and of incipient solidification (as obtained by cooling down after complete melting, and observing when cloudiness commenced); whilst those of *Bensemann* are (A) the temperature of complete liquefaction, when all turbidity disappears, as determined in the above described form of capillary tube, and (*B*) the somewhat lower temperature when the substance is sufficiently liquefied to run down in the capillary tube, but is not thoroughly melted to a limpid fluid :—

	Melting Point.				Solidifying Point.		
	Hübl.	Bensemann. A.	B.	Allen	Hübl.	Bach.	Allen.
	° C.	° C.	° C.	° C.	° C.	° C.	° C.
Olive oil, . . .	26·0	26 to 27	23 to 24	26·0	21·2	22·0	21·0
Almond oil, . .	14·0	...	...	...	5·0	...	...
Earth-nut oil, .	27·7	34 to 35	31 to 32	29·5	23·8	31·0	28·0
Rape oil, . . .	20·1	21 to 22	18 to 19	19·5	12·2	15·0	18·5
Cotton-seed oil, .	37·7	42 to 43	39 to 40	35·0	30·5	35·0	32·0
Sesamé oil, . .	26·0	29 to 30	25 to 26	23·0	22·3	32·5	18·5
Linseed oil, . .	17·0	...	...	24·0	13·3	...	17·5
Poppy oil, . . .	20·5	...	...	..	16·5	...	...
Hemp-seed oil, .	19·0	...	...	...	15·0	...	...
Walnut oil, . .	20·0	...	...	...	16·5	...	...
Castor oil, . . .	13·0	...	...	...	3·0	2·0	...
Palm oil, . . .	47·8	...	...	50·0	42·7	...	45·5
Coconut oil, .	24·6	...	...	24·0	20·4	...	20·5
Japan wax, . .	...	...	...	56·0	...	...	53·0
Myrtle wax, . .	...	...	...	47·5	...	...	46·0
Lard, ...	...	...	...	44·0	...	42	39·0
Tallow, ...	45·0	...	...	...	43 to 50	44 to 49	...
Shea butter, . .	39·5	...	...	...	38·0	...	...

The following tables by *Heintz*[1] represent the melting points of various definite mixtures of fatty acids :—

Mixtures of Myristic and Lauric Acids.

Melting Point.	Solidification Point.	Percentage of	
		Myristic Acid.	Lauric Acid.
° C.	° C.		
58·8	...	100	0
51·8	47·3	90	10
49·6	44·5	80	20
46·7	39·0	70	30
43·0	39·0	60	40
37·4	35·7	50	50
36·7	33·5	40	60
35·1	32·3	30	70
38·5	33·0	20	80
41·3	36·0	10	90
43·6	...	0	100

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[1] *Poggendorff Annalen*, xcii., 588.

Mixtures of Palmitic and Myristic Acids.

Melting Point.	Solidification Point.	Percentage of	
		Palmitic Acid.	Myristic Acid.
°C.	°C.		
62·0	...	100	0
61·1	58·0	95	5
60·1	55·7	90	10
58·0	53·5	80	20
54·9	51·3	70	30
51·5	49·5	60	40
47·8	45·3	50	50
47·0	43·7	40	60
46·5	43·7	35	65
46·2	44·0	32·5	67·5
46·2	43·7	30	70
49·5	41·3	20	80
51·8	45·3	10	90
53·8	...	0	100

Mixtures of Stearic and Palmitic Acids.

Melting Point.	Solidification.	Percentage of	
		Stearic Acid.	Palmitic Acid.
°C.	°C.		
69·2	...	100	0
67·2	62·5	90	10
65·3	60·3	80	20
62·9	59·3	70	30
60·3	56·5	60	40
56·6	55·0	50	50
56·3	54·5	40	60
55·6	54·3	35	65
55·2	54·0	32	67·5
55·1	54·0	30·5	70
57·5	53·8	20	80
60·1	54·5	10	90
62·0	...	0	100

Mixtures of Stearic and Myristic Acids.

Melting Point.	Percentage of	
	Stearic Acid.	Myristic Acid.
° C.		
69·2	100	0
67·1	90	10
65·0	80	20
62·8	70	30
59·8	60	40
54·5	50	50
50·4	40	60
48·2	30	70
47·8	20	80
51·7	10	90
53·8	0	100

Mixtures of Stearic and Lauric Acids.

Melting Point.	Percentage of	
	Stearic Acid.	Myristic Acid
° C.		
69·2	100	0
67·0	90	10
64·7	80	20
62·0	70	30
59·0	60	40
55·8	50	50
50·8	40	60
43·4	30	70
38·5	20	80
41·5	10	90
43·6	0	100

Mixtures of Palmitic and Lauric Acids.

Melting Point.	Percentage of	
	Palmitic Acid.	Lauric Acid.
° C.		
62·0	100	0
59·8	90	10
57·4	80	20
54·5	70	30
51·2	60	40
47·0	50	50
40·1	40	60
38·3	30	70
37·1	20	80
41·5	10	90
43·6	0	100

Hehner and *Mitchell*[1] repeated Heintz's[2] experiments in the case of stearic and palmitic acids, and obtained results in substantial agreement with his, taking into account the fact that their initial acids had both somewhat lower melting points.

Melting Points of Mixtures of Stearic and Palmitic Acids.

Stearic Acid.	Palmitic Acid.	Heintz Melting Point.	Hehner and Mitchell.
Per cent.	Per cent.	° C.	° C.
100	0	69·2	68·5
90	10	67·2	66·5
80	20	65·3	64·2
70	30	62·9	61·5
60	40	60·3	59·4
50	50	56·6	55·6
40	60	56·3	55·5
32·5	67·5	55·2	54·5
30	70	55·1	54·2
20	80	57·5	56·5
10	90	60·1	59·0
0	100	62·0	61·8

A more recent series of determinations of the melting and solidification points of pure stearic, palmitic, and oleic acids (iodine value = 90·5) were made by *Carlinfanti* and *Levi-Malvano*,[3] who used Dalican's method (*infra*) with an apparatus similar to that employed in cryoscopic determinations. The following results were obtained :—

Stearic Acid.	Palmitic Acid.	Beginning of Crystallisation.	Stearic Acid.	Oleic Acid.	Beginning of Crystallisation.	Palmitic Acid.	Oleic Acid.	Beginning of Crystallisation.
P. c.	P. c.	°C.	P. c.	P. c.	°C.	P. c.	P. c.	°C.
100	0	68·2	0	100	9·00	100	0	61·00
90	10	65·9	5	95	23·45	90	10	59·20
		(end, 61·5)	15	85	34·25	80	20	57·30
80	20	63·5	25	75	46·60	70	30	55·10
70	30	60·80	35	65	51·90	60	40	52·60
		(end, 57·0)			(end, 34·0)			(end, 44)
60	40	57·65	46	54	55·95	50	50	49·75
52·5	47·5	56·0	55	45	58·65	40	60	46·25
		(end, 56·0)			(end, 45)	30	70	41·60
50	50	56·25	65	35	61·25	20	80	35·00
40	60	55·90	75	25	63·40	10	90	24·80
30	70	54·75			(end, 57)	0	100	9·00
		(end, 54·79)	85	15	65·40			
20	80	55·75	95	5	67·15			
10	90	58·40	100	0	68·20			
5	95	59·60						
1	100	61·00						

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[1] *Analyst*, 1896, xxi., 369.

[2] *Ann. Chem. Pharm.*, xcii., 295.

[3] *Gazz. Chim. Ital.*, 1909, xxxix., 353.

From these results the conclusion was drawn that mixtures of stearic and palmitic acids form four series of solid solutions and one addition compound, which would correspond to the old margaric acid, to the more recent daturic acid, and, possibly, to the synthetical margaric acid of Heintz and Krafft. In the case of mixtures of stearic acid or palmitic acid with oleic acid, however, only a single series of solid solutions is formed.

The results obtained with mixtures of all three acids grouped in different systems were as follows :—

Stearic Acid.	Palmitic Acid.	Oleic Acid.	Beginning of Crystallisation.
Per cent.	Per cent.	Per cent.	°C.
74·5	13	12·5	62·30
66	17	17	60·15
61	19·5	19·5	58·80
51	24·5	24·5	55·60
29	35·5	35·5	48·65
12	44	44	45·15
80	3	17	64·10
74	4	22	62·80
69	4·5	26·5	61·65
63·5	5·5	31	60·40
57·5	6·5	36	58·65
51·5	7·5	41	56·90
46	8	46	55·10
41	7·5	51·5	53·30
91·5	7·5	1	65·60
80	17·5	2·5	63·00
69	27·5	3·5	60·10
57	38	5	56·30
46	48	6	54·60
34·5	58·5	7	53·80
27·5	64	8·5	52·70
23	68·5	8·5	52·70
12	78·5	9·5	55·05
40·5	55	4·5	54·80

Stearic Acid.	Palmitic Acid.	Oleic Acid.	Beginning of Crystallisation.
Per cent.	Per cent.	Per cent.	°C.
58·5	19·5	22	58·10
47	31	22	53·70
41	36·5	22·5	52·00
39	39	22	51·65
35	43	22	51·65
31	47	22	50·30
27·5	50·5	22	50·90
24	54	22	50·30
19·5	58·5	22	50·10
15·5	62	22·5	50·70
8	70	22	53·30
40·5	13·5	46	52·55
32·5	21·5	46	48·20
29	25	46	46·50
27	26·5	46	46·10
21·5	32	46·5	45·40
16·5	37·5	46	44·70
5·5	48·5	46	47·30
24·5	8	67·5	44·95
19·5	12·5	68	40·85
14·5	18	67·5	38·20
10	22·5	67·5	36·90
3	29	67·5	38·85
5·5	77·5	19·5	54·85
8	66	26	52·40
20	30·5	49·5	44·55

By plotting these results in diagrammatic form and calculating the amount of oleic acid from the iodine value the proportion of palmitic and stearic acids in a commercial mixture of the three acids may be calculated. In doubtful cases the method may be used in association with an estimation of the stearic acid by Hehner and Mitchell's method.

De Visser[1] found that stearic acid crystallised fifty times melted at 69·32° C., and palmitic acid at 62·618° C. He plotted curves of the

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[1] *Chem. Centralbl.*, 1898, ii., 176.

solidification points of different mixtures of the two acids. These showed two breaks—viz., at 54 and 47 per cent. of stearic acid. The lowest melting point observed (54·8175° C.) was given by a mixture containing 29·76 per cent. of stearic acid.

These tables amply illustrate the peculiarity above referred to in cases where mixtures are heated—viz., that the melting point of the mixture is almost invariably lower than that calculated from the relative proportions and melting points of the ingredients, and in certain cases falls below the melting point of the most fusible of the ingredients. Thus, in the case of a mixture of myristic and lauric acids containing equal quantities (50 per cent.) of each, since the ingredients melt respectively at 58·8° and 43·6° C., the melting point of the mixture would *a priori* be expected to be $\frac{58{\cdot}8 + 43{\cdot}6}{2} = 51{\cdot}2^\circ$; whereas it actually is 37·4°, or 13·8° lower than the calculated temperature, and 6·2° lower than the melting point of the most fusible ingredient.

Twitchell's Method.—It was shown by *Heintz*[1] that the depression of the melting point on adding one of the higher fatty acids to another was practically proportional to the amount of added acid, and but little affected by its nature, since the molecular weights of the fatty acids in most fats do not differ greatly.

Twitchell[2] has based a method of approximately estimating the composition of mixtures of fatty acids on this observation, a definite quantity of the mixture being added to a pure fatty acid, and the depression of the melting point of the latter determined. In experiments with pure fatty acids it was found that the melting point of stearic, palmitic, or behenic acids was depressed from 1·91° to 2·17° C. by the addition of 10 per cent. of one of the other acids or of oleic acid, or a mixture of these, and by 3·93 to 4·54 per cent. by the addition of 20 per cent.

For example, in applying the method to the examination of cottonseed oil fatty acids, the solid fatty acids (separated by the lead ether method) and the hydrogenated acids were added in weighed proportions to stearic, palmitic, and behenic acids respectively, and the depression observed. Thus the addition of 20 per cent. of a sample of cotton-seed oil fatty acids to 80 per cent. of palmitic acid depressed the melting point of the latter by 3·18 per cent., which would correspond with a mixture of 84·6 parts of palmitic and 15·4 parts of other fatty acids. Hence the fatty acids examined contained 4·6 parts of palmitic acid, or 23 per cent. The hydrogenated fatty acids mixed with pure stearic acid depressed the melting point of the latter so little that they must have contained 71 per cent. of stearic acid, corresponding to the same proportion of unsaturated fatty acids with 18 carbon atoms in the original mixture. On the other hand, they contained no more palmitic acid than was present before hydrogenation, so that unsaturated fatty acids with 16 carbon atoms could not have been present.

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[1] *Pogg. Annalen*, 1854, xcii., 588.

[2] *J. Ind. Eng. Chem.*, 1914, vi., 564.

Dalican's Method.—The following table by *Dalican*[1] represents the solidifying points of various mixtures of free "stearic" and "oleic" acids, analogous to those obtained by saponifying tallow completely and separating the fatty acids from the soaps formed. Twenty grammes of the fatty acid were then melted in a test-tube which was fitted into the neck of a large flask, and allowed to cool slowly. When incipient solidification became visible the contents of the tube were stirred with the thermometer with a rotary movement three times from right to left, and three times in the opposite direction. During this stirring the thermometer usually fell slightly just at first, but in every case rose again to a point at which the temperature remained stationary for about two minutes, the disengagement of latent heat during solidification balancing the loss of heat by radiation and convection, etc. The temperatures quoted are the stationary ones thus observed with the various mixtures examined. The joint percentages given in the table only add up to 95, the average yield of total fatty acids from tallow being taken as 95 per cent., after allowing for small quantities of water present and loss of weight by elimination of glycerol (*vide* Chap. VIII.) :—

Temperature.	"Stearic" Acid.	"Oleic" Acid.	Temperature.	"Stearic" Acid.	"Oleic" Acid.
° C.			° C.		
40	35·15	59·85	45 5	52·25	42·75
40·5	36·10	58·90	46	53·20	41 80
41	38 00	57 00	46·5	55·10	39·90
41·5	38·95	56·05	47	57 95	37·05
42	40·90	54·10	47·5	58 90	36·10
42·5	42 75	52·25	48	61·75	33·25
43	43·70	51·30	48·5	66·50	28·50
43·5	44·65	50·35	49	71·25	23·75
44	47·50	47·50	49·5	72·20	22·80
44·5	49·40	45·60	50	75·05	19·95
45	51·30	43·70			

The method of manipulation thus employed by Dalican is applicable in the case of most other substances the solidifying point of which is required; but the amount of rise indicated by the thermometer above the temperature of incipient solidification varies considerably in different cases, a constant temperature for two minutes or more not being always attained. *Finkener*[2] finds that the results are more concordant if the vessel containing the melted fatty matter is enclosed in an envelope of wadding, or jacketed with a wooden envelope, so as to diminish the rate of cooling.

A still better means of preventing the loss of heat is to use a small vacuum-jacketed tube, as in Hehner and Mitchell's method of determining the bromine thermal value (*q.v*). To obtain concordant results it is essential to use the same apparatus and method of working.

[1] *Mon. Scientif.*, Paris, 1868.

[2] *J. Soc. Chem. Ind.*, 1889, viii., 423; 1890 ix., 1071.

De Schepper and *Geitel* give the following table representing the amounts of mixed solid fatty acids of different solidification points practically obtainable from tallow, when these acids are separated from oleic acid to such an extent as to possess the solidification points named :—

Solidifying Point of Tallow Fatty Acids.	Percentage of "Stearine" (Solid Fatty Acids) of Solidification Point.			
° C.	48° C.	50° C.	52° C.	54·8° C.
10	3·2	2·7	2·3	2·1
15	7·5	6·6	5·7	4·8
20	13·0	11·4	9·7	8·2
25	19·2	17·0	14·8	12·6
30	27·9	23·2	21·4	18·3
35	39·5	34·5	30·2	25·8
40	57·8	49·6	43·5	37·0
42	66·6	57·6	50·5	42·9
44	77·0	66·2	58·4	49·8
46	87·5	75·8	67·0	56·8
48	100·0	87·2	76·6	65·0
50	...	100·0	87·0	74·5
52	...	...	100·0	84·8
54	...	...	...	95·3
54·8	...	...	...	100·0

The same authors give the following analogous table for the relative amounts of mixed solid fatty acids practically obtainable from palm oil :—

Solidifying Point of Palm Oil Fatty Acids.	Percentage of "Stearine" (Solid Fatty Acids) of Solidification Point.			
° C.	48° C.	50° C.	52° C.	55·4° C.
10	4·2	3·6	3·2	2·6
15	10·2	9·8	7·8	6·6
20	17·4	15·0	14·4	11·0
25	26·2	22·4	19·3	16·2
30	34·0	30·5	26·6	22·3
35	45·6	40·8	35·8	29·8
40	63·0	55·2	48·6	40·6
42	70·5	62·2	55·2	45·5
44	79·2	70·2	62·0	51·4
46	89·4	78·8	69·8	57·8
48	100·0	88·0	78·6	65·0
50	...	100·0	89·6	73·4
52	...	...	100·0	82·8
54	...	...	...	92·2
55·4	...	...	...	100·0

The following table[1] gives the Dalican figures and iodine values of the fatty acids of a number of solid fats:—

Fatty Acids of	Iodine Value.	Dalican Number.
		° C.
Oleo-margarine,	51·6	42
Butter, I.,	34·25	30·5
,, II.,	36·5	34·5
,, III.,	30·18	39·2
,, IV.,	...	38·5
Margarine,	38	43·2
Lard, I.,	69·3	37·5
,, II.,	74·13	36
,, II., + 10 per cent. Beef stearine,	62·57	41·0
,, III.,	63·89	36
,, IV.,	...	38
,, V.,	60·0	38·5
,, VI.,	60·2	40·0

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[1] Mitchell, *Unpublished.*

CHAPTER V.

SPECIFIC GRAVITY AND VISCOSITY.

SPECIFIC GRAVITY OF OILS, FATS, ETC.

Inasmuch as the majority of natural oils, fats, and similar substances are mixtures of more than one constituent, the relative proportions, and even the nature of the ingredients being subject to some degree of variation, it results that the general physical characters of any given oil, etc., are liable to fluctuation within certain limits. This is particularly the case with the specific gravity of such materials, differences in the climate and soil in which seed-bearing plants are grown, in the degree of cultivation and the maturity of the crop and such like causes often producing measureable differences in the relative density of the oil extracted; as also, to some extent, does the method of extraction adopted, the first runnings obtained by pressure in the cold being often perceptibly lighter bulk for bulk than those obtained later by hot pressure. In similar fashion, variations in the particular breed of animal (*e.g.*, in the case of oxen and sheep), the part of the body from which the fat is extracted, the mode of feeding, etc., often correspond with analogous fluctuations in the case of animal fats; added to which, the method of refinement adopted and the degree of purification effected, cause variations in proportion to the amount of residual mucilaginous or albuminous matters left unremoved; whilst the age of the sample is often a material point, many kinds of oil having a tendency to absorb oxygen from the air, thereby becoming more dense.

Notwithstanding these sources of variation, however, it is often possible to obtain useful information as to the freedom or otherwise of oils, etc., from admixture with adulterating substances by determining their specific gravity; or, in many cases, preferably, the specific gravity of the free fatty acids which they yield by saponification.

Pycnometers.—This determination is most accurately effected by means of a *pycnometer* [1] (*specific gravity bottle* or *Sprengel's tube*). With

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[1] For a description of some highly accurate forms of this instrument and their mode of use, together with a discussion of the corrections indispensable when results are required to be accurate to a unit in the fourth decimal place (± 0·0001), and *a fortiori* to one in the fifth place (± 0·00001) *vide* a paper by Alder Wright, *J. Soc. Chem. Ind.*, 1892, xi., 297.

the *Sprengel's tube* (Fig 15) in particular a very high degree of accuracy is readily attained. It consists of a U-tube with its ends drawn out to the diameter of capillary tubes and bent at right angles. In using it the oil is drawn up into it by suction, care being taken to exclude all air-bubbles, and the tube then immersed in a beaker of water at the required temperature for about ten minutes, after which a piece of filter-paper is applied to one of the capillary arms so as to withdraw sufficient oil to cause the meniscus of that in the other capillary arm to correspond exactly with a mark. In certain cases the temperature of the water causes the oil to contract beyond this mark, and it is then necessary to apply a drop of the oil on the end of a rod to the opening of other arm. Finally, the ends of the tube are closed by means of glass caps, and the tube itself wiped with a duster and weighed. The weight of the oil divided by the weight of water, which has been treated in exactly the same way in the Sprengel's tube, gives the specific gravity.

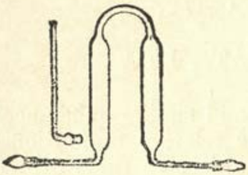
Fig. 15.—Sprengel's Tube.

Specific Gravity of Solid Fats and Waxes.—The specific gravity of solid fats and waxes is most frequently determined at a high temperature (100° C.), but several methods have been devised for obtaining the value at the ordinary temperature, and some of these are very useful, especially in the examination of beeswax.

Gintl[1] has devised a special form of pycnometer for the purpose. This consists of a cylindrical thin glass vessel, which fits into a frame with a screw at the top, by means of which glass covers at the top and the bottom can be held tightly in position. The apparatus is first weighed empty, and then filled with water at a standard temperature. It is then dried, filled with the melted fat or wax, allowed to cool to the same temperature, and again weighed.

Hager melts the wax, allows it to fall into cold strong alcohol, and then immerses these globules in dilute alcohol, which is further diluted or strengthened until they exactly float in the liquid, which will then be of the same gravity as the fat or wax.

It was pointed out by *Chattaway* and *Allen* that certain waxes undergo abnormal contraction when thus suddenly dropped into alcohol, and they prefer to use fragments of the wax which has been melted and allowed to cool spontaneously in a watch-glass.

A modification of Hager's method, which has given good results in the hands of Hehner and of the writer, consists in pouring the melted wax into a small cylinder made from glass tubing and left open at each end, the lower end being placed upon a glass plate. As soon as the wax has solidified, the outside of the glass is gently warmed and the solid core of wax pushed out and allowed to stand at the required temperature. Finally, it is brushed over with dilute alcohol to prevent air bubbles, and immersed in a mixture of alcohol

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[1] *Dingler's polyt. J.*, cxciv., 42.

and water, which is diluted or strengthened until the wax neither falls to the bottom nor rises to the surface of the liquid.

Aræometers and Hydrostatic Balancers.—For many purposes, where extreme accuracy is unnecessary, simpler instruments are often sufficient for the purpose in view, more especially when standardised or "calibrated," as described below.

Thus, for most fluid oils the indications of a fairly well made *aræometer* (hydrometer), used at a standard temperature, are sufficiently accurate; whilst either for ordinary temperatures or for more elevated ones, the *hydrostatic balance* is extremely convenient. In using this latter instrument at higher temperatures (*e.g.*, near that of boiling water), it should not be forgotten that if the plummet immersed in the liquid to be examined (as shown in Figs. 16 and 17) be made of glass, it will displace more than 0·2 per cent. (or upwards of 2 per thousand) more fluid at near the boiling point of water than at 15° C.,[1] so that if originally constructed to give accurate indications at 15°, the values indicated at near 100° will be more than 2 per thousand too high on account of the great displacement. Hence, in the case of fluid oils, the specific gravity of which is usually from 0·9 to 0·95, the indications at near 100° C. will be approximately 0·002 too

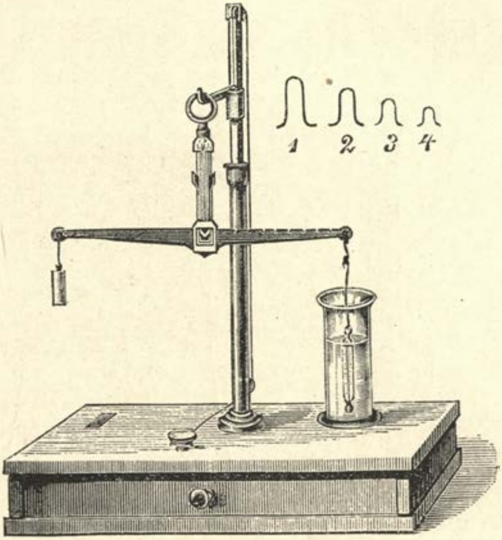

Fig. 16.—Mohr's Hydrostatic Balance.

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[1] The cubical coefficient of expansion of glass approximates $0\cdot000025 = \frac{1}{40,000}$; so that a rise of temperature of 85° represents an increase in volume of $\frac{85}{40,000} = 2\cdot125$ per thousand.

high. Analogous errors of excess apply to all glass aræometers and pycnometers when graduated at one temperature and used at a higher one.

Another matter to be remembered is that of the numerical value arrived at expresses different things, according as the water with which the instrument is graduated is at one temperature or another; this applies equally to the indications of the pycnometer, the aræometer, and the hydrostatic balance. When the indications represent the ratio between the weight of a given volume of substance and that of the same weight of water, *both at the same temperature t*°, the value is the *specific gravity at t*°. Thus the specific gravity at 100° C. of a given oil or melted wax is the weight of a given volume of substance compared with that of the same weight of water also at 100° C. If, however, the oil be at *t*°, and the water at a different temperature, T, the value is neither the specific gravity at *t*° nor that at T. If T = 4° C., the value is *the weight in grammes at t° of* 1 *c.c. of oil*, since at 4° C. 1 c.c. of water weighs 1 gramme; this value is often considerably different from the specific gravity of the oil at *t*°, the more so the higher the value of *t*. Thus if *t* = 100° C., since 1 c.c. of water at 100° weighs 0·9586 gramme, the weight of 1 c.c. of oil at 100° C. will be only 0·9586 times the specific gravity of the oil at 100° C.; *i.e.*, the latter value is more than 4 per cent. in excess of the former one. Unfortunately, most observers have recorded their results in neither of these two forms, but have used a mode of expression where T is not 4°, and is not = *t*. The result thus expressed is *the relative density of water*

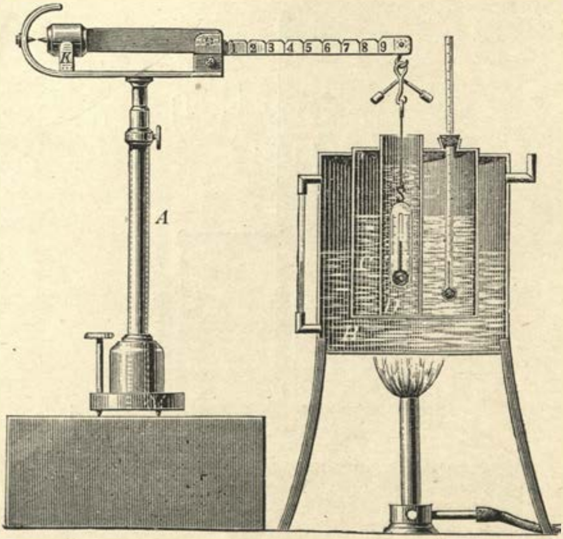

Fig. 17.—Westphal's Hydrostatic Balance.

at t referred to water at T, sometimes expresses the relative density at $\frac{t}{T}$. When T = 15·5° C., a temperature frequently chosen, this value represents 1·0009 times the weight of 1 gramme of oil at $t°$, since 1 c.c. of water at 15·5 weighs 0·9991 gramme.

Lefebre's Oleometer.—Fig. 18 represents Lefebre's oleometer, which is specially marked for oils, the specific gravity of which at 15·5° ranges from 0·9 to 0·95. This instrument is so graduated that when immersed in a fluid at the standard temperature of 15·5° C. the specific gravity is directly read off. At various points the average specific gravities of normal oils of different kinds are marked off (linseed oil, olive oil, etc.); and, as a rule, to save figures, only the second and third decimal places are given—*i.e.*, 35 indicates 0·935, 8 represents 0·908, and so on. If the temperature differ slightly from the normal one of 15·5°, a correction is made by adding (or subtracting) $\frac{2}{3} \times 0{\cdot}001$ for every degree of temperature above (or below) the standard, this correction being based on the fact that most oils expand on heating to nearly the same extent, so that the specific gravity becomes lowered by about 0·00068 per 1° C. (*vide infra*).

When it is required to determine the specific gravity of an oil, etc., at a temperature somewhat elevated (say at near 100° C.), some form of heating arrangement must be employed, whereby the vessel containing the oil, etc., can be constantly maintained at the required temperature for some time. Fig. 17 illustrates a form of hot-water bath thus used for a *Westphal hydrostatic balance*.

When temperatures other than 100° C., but higher than the ordinary atmospheric temperatures are required, the hot air arrangement indicated by

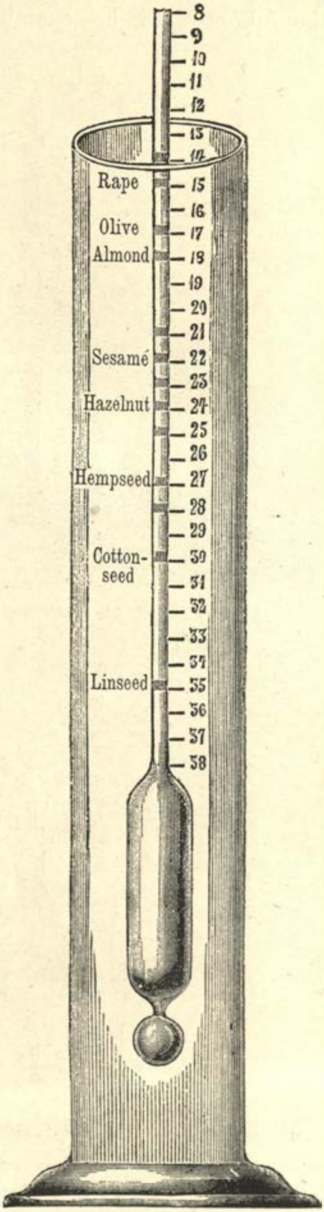

Fig. 18.—Lefebre's Oleometer.

Fig. 19 may be employed. In this case the vessel C, containing the oil, etc., to be examined, is heated by a hot-air bath, B,

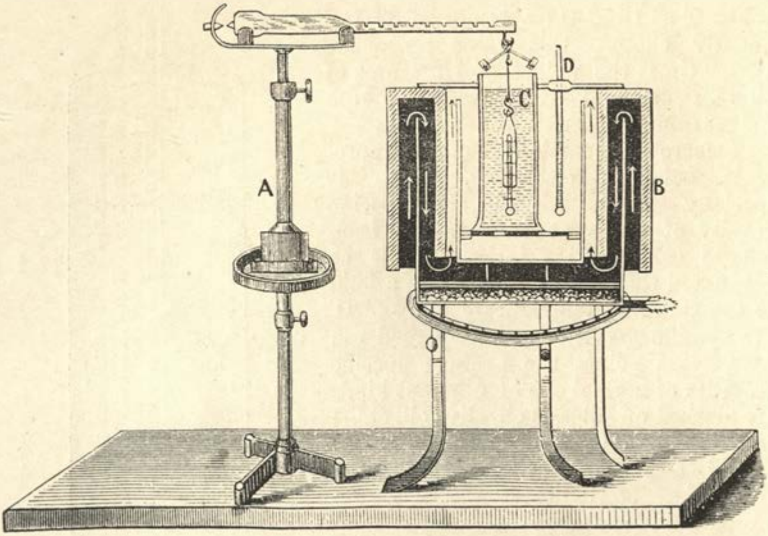

Fig 19.—Hot-Air Bath for use with Westphal's Hydrostatic Balance.

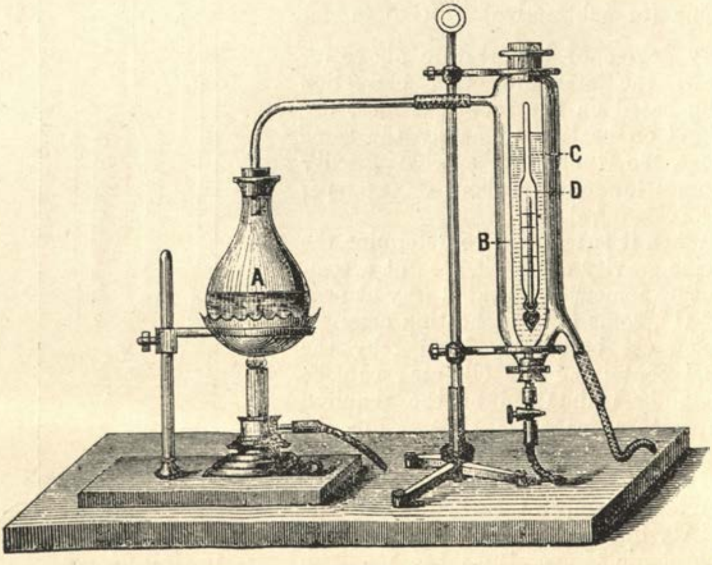

Fig. 20.—Ambühl's Arrangement.

the ascending hot gases from a ring burner being made to circulate as indicated by the arrows. The temperature of the inner hot-air space is shown by the thermometer, D, and should not differ much from that of the oil itself, as indicated by a thermometer immersed therein (in the figure, as also in Fig. 17, this is enclosed inside the plummet[1]). A thermostat, or heat regulator where the gas supply is automatically regulated, should be employed in addition.

Fig. 20 represents Ambühl's arrangement, in which the vessel containing the oil is heated in a current of vapour (steam from boiling water, or other vapour emitted by a fluid of convenient boiling point).

Thermal Aræometer.—In the Paris Municipal Laboratory, a peculiar kind of "thermal aræometer," constructed by Langlet, is in use for the examination of olive oil. This is an aræometer with an internal thermometer, so adjusted that when the instrument is placed in pure olive oil the level of the fluid indicated on the stem and the thermometer reading are practically the same. If the oil be warmed so as to become lighter, the hydrometer sinks to an increased depth, and the thermometer column rises through the same length, so that the two readings always correspond. If, however, the oil be not genuine olive oil, but contain an admixture of other oil of different density, the readings are stated not to agree. Thus, the following pairs of readings correspond with certain oils other than olive oil and various mixtures (*Muntz*) :—

	Thermometer Reading.	Reading on stem.
	°C.	°C.
Earth-nut oil, ...	18·9	11·0
Cotton-seed oil, ...	18·9	10·5
3 parts olive oil to 1 of cotton-seed oil, . .	18·1	16·1
2 ,, ,, 1 ,, ,, . .	18·6	15·8
3 ,, ,, 1 of sesamé oil, . .	18·3	16·5
2 ,, ,, 1 ,, . . .	18·6	16·1
3 ,, ,, 1 of colza oil, . . .	18·3	18·5
3 ,, ,, 1 of earth-nut oil, . .	18·1	17·2
2 ,, ,, 1 ,, . .	18·7	17·5
52 ,, ,, 48 ,, . .	18·7	17·4

CONSTRUCTION OF TABLES OF ERRORS FOR HYDROMETERS AND HYDROSTATIC BALANCES.

Hydrometers, as usually sold, are not infrequently affected by errors of construction and graduation, sufficiently great to render their indications inexact to at least ± one unit in the third decimal place, and sometimes much more, quite apart from any error arising from

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[1] Fletcher has recently constructed a *thermohydrometer*, consisting of an ordinary aræometer with enclosed thermometer, so as to read off the temperature of the fluid examined simultaneously with the indicated relative density.

the difficulty of reading off the exact level. To do this with as little error as possible, the hydrometer should be floated in a jar with a white strip of enamel at its back, or a strong light so placed that the lowest point of the meniscus formed by the upper part of the fluid can be read off on the hydrometer scale. Unless the fluid examined be excessively dark in colour, this can generally be done pretty readily, the eye being level with the bottom of the meniscus (as in reading a burette).

To eliminate, as far as possible, errors of graduation, it is necessary to construct for each instrument a table of errors, obtained by directly comparing at the same temperature the values given by different fluids simultaneously examined by means of an accurate pycnometer, and with the hydrometer. The following illustration will suffice to indicate the mode of construction of such a table of errors for a hydrometer intended to show at 15·5° C. values ranging between 0·900 and 0·950; when such a table is carefully prepared, the corrected reading of a tolerably sensitive hydrometer should be exact within ± two, or even ± one unit in the fourth decimal place. The figures are expressed on the thousandfold scale,[1] three comparisons being made respectively near the top, middle, and bottom of the hydrometer scale.

True Specific Gravity at 15·5° C. by Pycnometer.	Hydrometer Reading at 15·5° C.	Difference.
948·4	947·5	+ 0·9
924·7	925·0	– 0·3
901·1	902·5	– 1·4

From these comparisons the following table of errors is obtained by interpolation :—

Hydrometer Reading at 15·5° C.	Correction to be added to obtain the True Specific Gravity.	Corrected Specific Gravity at 15·5° C.
900·0	–1·50	898·5
905·0	–1·25	903·75
910·0	–1·00	909·0
915·0	–0·75	914·25
920·0	–0·50	919·5
925·0	–0·30	924·7
930·0	–0·05	929·95
935·0	+0·20	935·2
940·0	+0·45	940·45
945·0	+0·75	945·75
950·0	+1·00	951·0

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[1] To save decimals, specific gravity values are often quoted after multiplication by 1,000. Thus, an oil of specific gravity 0·967 is said "to have the gravity 967," and so on.

In similar fashion, a table of errors may be constructed for a hydrostatic balance. Thus, the following numbers were obtained with such an instrument of fairly good construction, the values being here expressed on the ordinary scale, and not multiplied by 1,000, the temperature throughout being 15·5° C. :—

True Specific Gravity by Pycnometer.	Value indicated by Hydrostatic Balance.	Difference.
0·9976	0·9995	− 0·0019
0·9517	0·9530	− 0·0013
0·9098	0·9100	− 0·0002
0·8524	0·8520	+ 0·0004

From these determinations the following table of errors is calculated by interpolation :—

Specific Gravity indicated by Hydrostatic Balance.	Correction to be added to obtain the True Specific Gravity.	Corrected Specific Gravity.
0·85	+ 0·0004	0·8504
0·86	+ 0·0003	0·8603
0·87	+ 0·0002	0·8702
0·88	+ 0·0001	0·8801
0·89	0	0·8900
0·90	− 0·0001	0·8999
0·91	− 0·0002	0·9098
0·92	− 0·0005	0·9195
0·93	− 0·0008	0·9292
0·94	− 0·0010	0·9390
0·95	− 0·0013	0·9487
0·96	− 0·0014	0·9586
0·97	− 0·0015	0·9685
0·98	− 0·0017	0·9783
0·99	− 0·0018	0·9882
1·00	− 0·0019	0·9981

Considerably larger corrections than most of those indicated in this table have sometimes to be applied to instruments as purchased, in order to obtain the true specific gravities from the direct results of observation.

Hydrometer Scales.—A considerable number of more or less arbitrary scales for aræometers are in use, a circumstance often leading to much practical inconvenience. The simplest or "gravity" scale is that in which the specific gravity of the fluid is directly indicated by the level to which the instrument sinks in the fluid (at the normal temperature)—*e.g.*, in Lefebre's oleometer (*q.v.*). Twaddell's scale is not much inferior in simplicity, each degree on that scale representing an alteration of 5 units in gravity on the thousandfold scale, and the valuation being given by the formula

$$S = 1{,}000 + 5n,$$

where S is the specific gravity on the thousandfold scale, and n the hydrometer reading. Thus 10° T. represents specific gravity 1·050; 100° T. specific gravity 1·500; 150° T. specific gravity 1·750; and so on. The same rule applies in the case of a fluid having a density less than that of water, the value of n being then negative, so that if $n = -10°$ T., the specific gravity would be 0·950, and so on. The negative-scale Twaddell hydrometer, however, is but rarely used. Several other scales are also in use, more especially in different parts of the Continent. The following table of formulæ is given by *Benedikt*, expressing the relative values of their degrees, S and n having the same meanings as above :—

Aræometer of	Temperature.	Fluids Heavier than Water.	Fluids Lighter than Water.
	Degrees.		
Balling, ...	17·5 C.	$S = \frac{200}{200 - n}$	$S = \frac{200}{200 + n}$
Beaumé, ...	12·5 C.	$S = \frac{144}{144 - n}$	$S = \frac{144}{134 + n}$
Beaumé,[1]	15·0 C.	$S = \frac{144{\cdot}3}{144{\cdot}3 - n}$	$S = \frac{144{\cdot}3}{134{\cdot}3 + n}$
Beaumé,[2]	17·5 C.	$S = \frac{146{\cdot}78}{146{\cdot}78 - n}$	$S = \frac{146{\cdot}78}{136{\cdot}78 + n}$
Beck, ...	12·5 C.	$S = \frac{170}{170 - n}$	$S = \frac{170}{170 + n}$
Brix, ...	12·5 R. 15·625 C.	$S = \frac{400}{400 - n}$	$S = \frac{400}{400 + n}$
Cartier, ...	12·5 C.	...	$S = \frac{136{\cdot}8}{126{\cdot}1 + n}$
Fischer, ...	12·5 R. 15 625 C.	$S = \frac{400}{400 - n}$	$S = \frac{400}{400 + n}$
Gay Lussac,[3] . . .	4 C.	$S = \frac{100}{n}$	$S = \frac{100}{n}$
E. G. Greiner, . . .	12·5 R. 15·625 C.	$S = \frac{400}{400 - n}$	$S = \frac{400}{400 + n}$
Stoppani,[4] . . .	12·5 R. 15·625 C.	$S = \frac{166}{166 - n}$	$S = \frac{166}{166 + n}$

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[1] $S = \frac{144{\cdot}3}{144{\cdot}3 + n}$ for lighter fluids (*Schädler*).

[2] $S = \frac{146{\cdot}78}{146{\cdot}78 + n}$ for lighter fluids (*Schädler*).

[3] $S = \frac{100}{100 - n}$ for heavier fluids, and $= \frac{100}{100 + n}$ for lighter ones (*Schädler*).

[4] $S = \frac{160}{160 - n}$ for heavier fluids, and $= \frac{160}{160 + n}$ for lighter ones (*Schädler*).

Lunge and *Hurter* (*Alkali Maker's Pocket-book*) regard the series of values found by means of the formula $S = \frac{144\cdot3}{144\cdot3 - n}$ as the only "rational" one of the various Beaumé scales in use; taking the formula at 15° C., the specific gravity of water at 15° C. = 0° B.; whilst 66° B. represents specific gravity $\frac{144\cdot3}{144\cdot3 - 66} = 1\cdot8426$. The following table exhibits the relationships between the values of "rational" Beaumé degrees, Twaddell degrees, and true specific gravity :—

Beaumé.	Twaddell.	Specific Gravity.	Beaumé.	Twaddell.	Specific Gravity.
0	0	1·000	36·0	66·4	1·332
0·7	1·0	1·005	38	71·4	1·357
1·0	1·4	1·007	40	76·6	1·383
1·4	2·0	1·010	42	82·0	1·410
2·0	2·8	1·014	44	87·6	1·438
2·7	4·0	1·020	46	93·6	1·468
4·0	5·8	1·029	48	99·6	1·498
5·0	7·4	1·037	50	106·0	1·530
6·7	10·0	1·050	52	112·6	1·563
8·0	12·0	1·060	54	119·4	1·597
10·0	15·0	1·075	56	127·0	1·635
14·0	21·6	1·108	58	134·2	1·671
16·0	25·0	1·125	60	142·0	1·710
18·8	30·0	1·150	61	146·4	1·732
20·0	32·4	1·162	62	150·6	1·753
23·0	38·0	1·190	63	155·0	1·775
25·0	42·0	1·210	64	159·0	1·795
27·0	46·2	1·231	65	164·0	1·820
30·0	52·6	1·263	66	168·4	1·842
33·0	59·4	1·297	67	173·0	1·865

RELATIVE DENSITIES OF THE PRINCIPAL OILS, FATS, ETC.

Many chemists have published the results of their determinations of the specific gravities of genuine oils, etc. In most instances the observed limits of variation in this respect are not very wide, being mainly dependent on the freedom from rancidity and free fatty acids; the degree of refinement (or freedom from mucilaginous matter, etc.): the age of the sample (whether oxygen has been absorbed or not), and so on. In many cases a measurable difference is observable between the density of the oil first expressed, especially when cold drawn, and that of the later portions obtained by the aid of heat, the latter being generally heavier. The following figures are given by *Schädler* as expressing the average values of the specific gravities at 15° C. of a large number of the more commonly occurring vegetable and other oils :—

Name of Oil.	Specific Gravity at 15° C.	Name of Oil.	Specific Gravity at 15° C.
Almond oil,	0·9190	Madia oil	0·9350
Arachis oil (earth-nut oil),	0·9202	Mustard oil,	0·9182
Bassia fat (Illipé butter),	0·9580	Maize oil,	0·9210
Ben oil,	0·9120	Nut oil (walnut oil,	0·9260
Belladonna-seed oil,	0·9250	Nutmeg oil,	0·9480
Beech-nut oil,	0·9225	Olive oil (greenish-yellow),	0·9144
Cameline oil (gold of pleasure),	0·9328	,, (best quality),	0·9177
		,, (Gallipoli),	0·9196
Cacao butter,	0·9000	Pine oil (red pine-seed oil; pinaster-seed oil),	0·9285
Castor oil,	0·9667		
Coconut oil,	0·9250	Palm oil,	0·9046
Colza oil,	0·9150	Poppy-seed oil,	0·9245
Cotton-seed oil (raw),	0·9224	Yellowhorn poppy oil,	0·9250
,, (refined),	0·9230	Plum-kernel oil,	0·9127
Croton oil,	0·9550	Radish-seed oil,	0·9162
Euonymus oil (spindle oil),	0·9380	Rape oil,	0·9157
Grape-seed oil,	0·9202	Red rape oil,	0·9282
Hemp-seed oil	0·9276	Winter rape oil.	0·9154
Gourd-seed oil,	0·9251	,, (refined),	0·9177
Hazel-nut oil,	0·9154	Sesamé oil,	0·9235
Linseed oil (raw),	0·9299	Sunflower-seed oil,	0·9262
,, (boiled).	0·9411	Tobacco-seed oil,	0·9232
Melon-seed oil,	0·9251	Weld seed oil,	0·9358

Animal Oils, etc.

Name of Oil.	Source.	Specific Gravity at 15° C.
Bone fat,	Bones,	0·9185
Cod-liver oil,	Gadus morrhua, &c.,	0·9200
,, (purified),	,, ,,	0·9270
,, (Labrador),	,, ,,	0·9237
Mutton tallow,	Sheep,	0·9147
Seal oil,	Phoca vitulina, &c.,	0·9246
,, (purified),	,, ,,	0·9261
Sperm oil,	Physeter macrocephalus,	0·9115
Whale oil (train oil),	Balæna mysticetus,	0·9250
,, (white),	,, ,,	0·9258

The following determinations of the specific gravity at 15° C. of various *solid* fats, etc., are given by *Hager* and *Dieterich* :—

	Hager.	Dieterich.
Beef tallow, ...	0·925 to 0·929	0·952 to 0·953
Sheep's tallow, ...	0·937 to 0·940	0·961
Hog's lard, ...	0·931 to 0·932	...
Stearine, ...	...	0·961 to 0·972
Stearic acid (melted), . . .	0·964	...
,, (crystallised), . .	0·967 to 0·969	...
Butter fat (clarified), . . .	0·938 to 0·940	...
,, (several months old), .	0·936 to 0·937	...
Artificial butter, ...	0·924 to 0·930	...
Cacao butter (fresh), . . .	0·950 to 0·952	0·980 to 0·981
,, (very old), . .	0·945 to 0·946	...
Beeswax (yellow), ...	0·959 to 0·962	0·963 to 0·964
,, (white), ...	0·919 to 0·925	0·973
Japan wax, ...	0·977 to 0·978	0·975
,, (very old), . . .	0·963 to 0·964	...
Spermaceti, ...	...	0·960
Colophony (American), . . .	1·100	1·108
,, (French), . . .	...	1·104 to 1·105
Galipot resin (purified), . . .	...	1·045
Crude ozokerite, ...	...	0·952
Ceresin (yellow), ...	0·925 to 0·928	0·922
,, (half white), . . .	0·923 to 0·924	0·920
,, (pure white), . . .	0·905 to 0·908	0·918

The following valuations of specific gravity at 37·8° C. = 100° F. are given by *Muter* [2] :—

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[2] Spon's *Encyclopædia of Arts and Manufactures*, ii., 1469. The values quoted are the numbers expressing the weights of given volumes of oil at 37·8° C., referred to the weight of the same volume of water at the same temperature as unity, and consequently are the pure specific gravities at 37·8° C. Muter, however, prefers to call them "actual densities"; an unfortunate term, as the figures are very different from the true densities.

Oil.	Limits of Specific Gravity.	Average.
Almond.	0·8980 to 0·9109	0·9056
Arachis (earth-nut), ...	0·9073 ,, 0·9020	0·9085
Castor, ...	0·9550 ,, 0·9576	0·9558
Coconut, ...	0·9103 ,, 0·9152	...
Cotton-seed (brown), . . .	0·9170 ,, 0·9197	0·9176
,, (refined—salad oil), .	0·9130 ,, 0·9140	0·9136
Cod-fish, ...	0·9114 ,, 0·9220	0·9176
Cod-liver, ...	0·9173 ,, 0·9180	0·9179
Hemp-seed, ...	0·9190 ,, 0·9195	0·9193
Lard, ...	0·9076 ,, 0·9082	0·9078
Linseed (raw), ...	0·9232 ,, 0·9300	0·9252
,, (boiled), ...	0·9320 ,, 0·9440	0·9380
Neat's foot, ...	0·9052 ,, 0·9079	0·9070
Nut, ...	0·9080 ,, 0·9090	0·9085
Olive, ...	0·9052 ,, 0·9079	0·9070
Poppy, ...	0·9150 ,, 0·9155	0·9154
Rape, ...	0·9060 ,, 0·9077	0·9067
,, refined (Colza), . . .	0·9053 ,, 0·9065	0·9067
Seal, ...	0·9136 ,, 0·9195	0·9179
Sperm, ...	0·8672 ,, 0·8963	0·8724
Whale, ...	0·9056 ,, 0·9066	0·9060

Since 1 c.c. of water weighs 1·0000 grm. at 4° C., 0·99908 at 15·5° C., and 0·9933 at 37·8° C., these values, when reduced to the standard of "specific gravity at 37·8° C. referred to water at 15·5° C." $\left(\text{specific gravity at } \frac{37{\cdot}8^\circ}{15{\cdot}5^\circ}\right)$, will be less in the proportion $\frac{0{\cdot}9933}{0{\cdot}99908}$, *i.e.*, less by 0·58 per cent.; that is, less by from ·0051 to ·0056. If reduced to the standard of "weight at 37·8° C. in grms. per c.c.," they will be less in the proportion $\frac{0{\cdot}9933}{1{\cdot}0000}$, *i.e.*, by ·67 per cent.; that is, less by from ·0058 to ·0064.

Classification of Oils, Fats, etc., according to their Relative Densities.—The following tables are given by *Allen*,[1] the relative density being

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[1] *Commercial Organic Analysis* (1899), II. (i.), 119.

taken at 15·5° C. in the case of liquid oils, and at $\frac{99^\circ}{15 \cdot 5^\circ}$ C. in the case of fats, solid or nearly so at ordinary temperatures :—

Oils Liquid at 15° C.

Class of Oil.	Specific Gravity at 15·5° C. = 60° F.				
	·875 to ·884.	·884 to ·912.	·912 to ·920	·920 to ·937.	·937 to ·970.
Vegetable oils.	None.	None.	Olive. Almond. Ben. Arachis. Rape. Colza. Mustard. *Essentially non-drying oils.*	Cotton-seed. Sesamé. Sunflower. Hazelnut. Poppy-seed. Hemp-seed. Linseed (raw). Walnut. Coconut. Oleine (manufactured). *More or less drying oils.*	Japanese wood (tung) oil. Croton. Castor. Linseed (boiled). Blown oils (manufactured).
Terrestrial Animal oils.	None.	None.	Neat's foot. Bone. Lard and tallow oils (manufactured.	None.	None.
Marine Animal oils.	Sperm. Bottlenose. Doegling.	None.	Shark-liver.	Whale. Porpoise. Seal. Menhaden. Cod-liver. Shark-liver.	None.
Free fatty acids.	None.	Oleic Acid.	...	Linolic acid.	Ricinoleic acid.
Hydrocarbon oils.	Shale products. Petroleum products.	Shale products. Petroleum products.	Heavy Petroleum products.	None.	None.

Oils, etc., Pasty or Solid at 15·5° C.= 60° F.

Arranged according to their Specific Gravity when Melted.

Class of Oil, &c.	Relative Density at $\frac{99°}{15·5°}$.[1]			
	·750 to ·800.	·800 to ·855.	·855 to ·863.	·863 to ·867.
Vegetable fats.	None.	None.	Palm oil. Cacao butter.	Palm-nut oil. Cocoa-nut oil. Japan wax. Myrtle wax. Cotton-seed "stearine."
Animal fats.	None.	None.	Tallow. Lard. Suet. Dripping. Bone fat. Margarine.	Butter fat. Compound lard.
Vegetable and Animal waxes.	None.	Spermaceti. Beeswax. Chinese wax. Carnauba wax.	None.	None.
Free fatty acids.	None.	Stearic acid. Palmitic acid. Oleic acid.	None.	None.
Hydrocarbons.	Paraffin wax. Ozokerite.	Shale products. Petroleum products.	Vaseline.	None.

Rosin oils and rosin are not included in these tables, these substances having specific gravities mostly higher than any therein mentioned—viz., from 0·97 to upwards of 1·0. Similar remarks apply to some of the highest-boiling petroleum and shale hydrocarbons.

Variation of Density of Oils, etc., with Temperature.—Like most other substances, oils and melted fats, etc., expand on heating. It is somewhat remarkable that nearly all bodies of this description expand at about the same rate (within not very wide limits of departure from the average), so that 1 c.c of substance always increases to about

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[1] These relative density values were for the most part taken with the plummet apparatus (Westphal's hydrostatic balance) and *not* corrected for the expansion of the glass plummet used ; many of the values are, therefore, about 0·2 per cent. too high—*i.e.*, too high by nearly 0·002.

Name of Oil or Fat, &c.	Ratio of Weight of a given Volume of Substance at $t°$, to that of the same Volume of Water at 15·5° considered as 1000.			Mean Variation per 1° Alteration in Temperature.
	t=15·5° C.	t=40°-80° C.	t=98°-99° C.	
Arachis oil (earth-nut oil), . .	922	...	867·3	0·66
Beeswax, ...	...	835·6 at 80°	822·1	0·75
Butter fat, ...	...	904·1 at 40°	867·7	0·62
Castor oil, ...	965·5	...	909·6	0·65
Cod-liver oil, ...	927·5	...	874·2	0·65
Cocoa-nut "oleine," . . .	926·2	...	871·0	0·67
,, "stearine," . .	...	895·9 at 60°	869·6	0·67
,, oil, ...	...	911·5 at 40°	873·6	0·64
Cotton-seed oil, ...	925	...	872·5	0·63
Doegling oil (bottlenose whale), .	880·8	...	827·4	0·64
Japan wax, ...	...	901·8 at 60°	875·5	0·69
Lard, ...	...	898·5 at 40°	860·8	0·65
Linseed oil, ...	935	...	880·9	0·65
Menhaden oll, ...	932	...	877·4	0·65
Neat's foot oil, ...	914	...	861·9	0·63
Niger-seed oil, ...	927	...	873·8	0·64
Palm butter, ...	...	893·0 at 50°	858·6	0·72
Porpoise oil, ...	926	...	871·4	0·65
Rape oil, ...	915	...	863·2	0·62
Seal oil, ...	924	...	873·3	0·62
Sesamé oil, ...	921	...	867·9	0·62
Spermaceti, ...	...	835·8 at 60°	808·6	0·72
Sperm oil, ...	883·7	...	830·3	0·65
Tallow, ...	...	895·0 at 50°	862·6	0·67
Whale oil, ...	930·7	...	872·5	0·70
Paraffin wax, ...	...	780·5 at 60°	753·0	0·72
Commercial "stearine" (crude stearic acid), ...	...	859·0 at 60°	830·5	0·75
Commercial "oleine" (impure oleic acid), ...	903·2	...	848·4	0·66

1·00075 c.c. by rise of temperature of 1° C. The effect of this is to diminish the density in the inverse proportion; so that an oil, etc., the specific gravity of which at 15° C. is from 0·9 to 0·95, will become diminished in specific gravity to $\frac{0·9}{1·00075}$ to $\frac{0·95}{1·00075}$ by rise of 1° in temperature—*i.e.*, the diminution in the specific gravity is 0·00067 to 0·00071. The preceding values were thus obtained by *A. H. Allen*.[1] For the sake of convenience, and to avoid decimals, all the figures are multiplied by 1,000.

From these values it results that whilst glyceridic oils fluid at the ordinary temperature diminish in specific gravity between 15° and

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[1] *Commercial Organic Analysis*, 1899, ii., (i.), 32, *et seq.* The values at the higher temperatures were mostly obtained by a plummet apparatus (Westphal's hydrostatic balance), and *not* corrected for the expansion of the glass plummet used, the object being simply to make comparative estimations. Hence many of the figures in the last column are somewhat too low by about ·01 to ·02.

98° C. at approximately the average rate of 0·64 per 1° (uncorrected for plummet expansion; somewhat more when corrected), glycerides of higher melting point (like Japan wax and palm butter) and waxes (beeswax, spermaceti, paraffin wax) diminish in specific gravity at a slightly higher rate, averaging about 0·7 per 1°. In all cases, however, the rate is sensibly near to $\frac{2}{3} \times 0{\cdot}001$ per 1° C., reckoned on the usual specific gravity scale (water = 1) and not multiplied by 1,000.

Figures closely in agreement with these have been subsequently obtained by other chemists. Thus, *C. A. Crampton*[1] obtained for various samples of lard, lard stearine, beef fat, oleostearine, cottonseed oil, and olive oil, coefficients of expansion between 15° and 100° C. varying from 0·000715 to 0·000797, and averaging about 0·00075. Since the relative density at $\frac{15°}{4°}$ of these substances was found to lie between 0·9065 and 0·9220, the average decrease in density per 1° C. rise in temperature was close to 0·69 on the thousand-fold scale.

W. T. Wenzell[2] found that olive oil, mustard-seed oil, castor oil, sperm oil, and cod-liver oil expanded to almost exactly the same extent in each case between 16·7° and 44·4° C. (62° and 112° F.); the increment in bulk being 2 per cent., all the substances being examined in the same dilatometer. This represents an apparent coefficient of expansion per 1° C. of 0·00072, which, when corrected for the expansion of the glass, becomes 0·00075, or practically the same figure as that found by *Crampton;* and indicating an average decrement in density per 1° C. rise in temperature of 0·68 to 0·69.

On the other hand, *Lohmann*[3] states that 1,000 volumes of olive oil increase by 0·83 volume for 1° C. rise of temperature; whilst the analogous increment for rape oil is 0·89, and for train oil 1·00; figures perceptibly higher than those found by the other observers above mentioned.

Wright[4] has calculated the average value for the expansion of any oil or fat so that the correction to be applied to the specific gravity for each variation of 1° C. from the standard temperature may be rapidly found by reference to the following table :—

°C.	Factor.	°C.	Factor.
10	0·99611	18	1·00177
11	0·99682	19	1·00248
12	0·99752	20	1·00319
13	0·99823	21	1·00391
14	0·99894	22	1·00462
15	0·99965	23	1·00534
16	1·00035	14	1·00605
17	1·00106	25	1·00677

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[1] *J. Soc. Chem. Ind.*, 1889, viii., 550; from *Amer. Chem. J.*, xi., 232.

[2] *Analyst*, 1890, xv., 14.

[3] Schädler's *Technologie der Fette und Oele*, 2nd ed., edited by Lohmann, p. 91.

[4] *J. Soc. Chem. Ind.*, 1907, xxvi., 513.

The specific gravity alters considerably when an oil undergoes oxidation, or becomes rancid, with the liberation of free fatty acids, as was clearly shown by some results of *Thomson* and *Ballantyne*[1] on olive and other oils.

In order partially to obviate these drawbacks *Archbutt* proposed to determine the specific gravity of the free fatty acids of oils instead of that of the oils themselves.

VISCOSIMETRY.

In order to obtain valuations of the so-called "viscosity" of oils, etc., as approximate measurements of their relative lubricating powers, two classes of methods are in use—viz., those in which the measurements are made by observing the mechanical effects produced by applying the oil, etc., between two conveniently arranged surfaces in motion with respect to one another; and those in which the oil to be examined is made to pass through a given tube or orifice, and the time of passage of a known quantity is noted. From the practical point of view, obviously the most valuable measurements of the kind are those obtainable by imitating as nearly as possible the conditions under which the lubricant is to be used—*i.e.*, the power of overcoming friction is best measured by a testing machine precisely similar to that for which the lubricant is required; quick moving spindles, rapidly revolving axles in journal boxes, or heavy slow moving shafting, etc., being employed as occasion requires. Such measurements, however, can only be properly carried out in comparatively large establishments, and are not at all adapted for use in laboratories where the chemical nature of the oils is investigated and their general characters tested. Accordingly, in these cases, methods of the second kind are now usually employed, since experience has shown that the comparatively small-sized mechanical testing machines of various kinds that have been invented for the purpose are apt to give results more discordant amongst themselves, and less faithfully representing the actual lubricating values of the substances examined, than those obtained by apparatus for the determination of "efflux velocity" (incorrectly designated "viscosity").

M'Naught's Pendulum Machine.—Of the numerous simpler forms of mechanical testing arrangements that have been proposed, one of the earliest (M'Naught's pendulum machine) is also one of the least unsatisfactory. This consists of two discs, the lower one provided with a raised edge and attached to a vertical spindle revolving in bearings, the upper one resting on a pivot. The space between the two discs is filled with the oil to be tested, and the lower one made to revolve at a given speed. The friction due to the oil would in time cause the upper disc to revolve too; but this motion is prevented by means of a projecting pin in contact with a pendulum. In consequence, more or less pressure on the pendulum is produced, diverting

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[1] *J. Soc. Chem. Ind.*, 1890, ix., 589; 1891, x., 30.

it from a vertical position, and this degree of displacement affords a measure of the resistance of the oil.

The "Mobility" Test.—*E. Weiss*[1] has devised an apparatus for determining the consistency of an oil, and calculates the "mobility" (*Beweglichkeit*) from the results. The apparatus consists of a small metal disc, about 10 cm. in diameter, which is made to revolve within the oil by means of clockwork, actuated by a weight, the number of revolutions in a given time depending on the consistency of the oil. The weight (usually about 1,147 grammes) is so chosen that the disc makes 150 revolutions in water at 15° C. in 30 seconds.

When the vessel is filled with a thick liquid and the driving weight varied, the resistance is proportional to the rapidity of the revolutions, or

$$\mathrm{P} = mu,$$

where P represents the driving force, u the number of revolutions in 30 seconds, and m a constant of the particular oil examined. In the case of rape oil the constant was found to be 64·27, whilst for more mobile liquids it was determined experimentally that, up to a weight of 2,500 grammes, the following formula was applicable :—

$$\mathrm{P} = a + bu^{\frac{3}{2}},$$

in which $a = 43{\cdot}5$, and $b = 0{\cdot}60853$.

For liquids whose consistency falls between that of water and rape oil, the formula is more complex, viz. :—

$$\mathrm{P} = \mathrm{A}\mu v_0(1 - a),$$

in which A is a constant depending on the dimensions of the apparatus, v_0 represents the rapidity of the revolution of the oil in the vicinity of the disc, μ is the coefficient of the friction of the liquid, and a denotes what fraction the rapidity of revolution near the surface of the liquid is of the rapidity of revolution near the disc.

For Engler's viscosimeter the law of Poiseuille holds good—

$$\mathrm{T} = \mathrm{B}\mu,$$

in which T represents the time taken by the liquid in running out, and B is a constant depending on the apparatus.

By incorporating this formula into the previous equation, *Weiss* obtains the formula

$$\mathrm{T}v_0 = \frac{\mathrm{PB}}{\mathrm{A}} \cdot \frac{1}{1 - a}.$$

If, then, in examining a number of oils, the same viscosimeter and consistency apparatus, and the same weight are invariably used, $\frac{\mathrm{P\,B}}{\mathrm{A}}$ has always the same value, and the product of the number of revolutions and of the time of efflux from the viscosimeter must be proportional to a constant $\frac{1}{1-a}$, which varies with the value of a.

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[1] *Dingler's polyt. J.*, 1898, cccix., 76.

Thus, a and Tv_0 furnish a measure of the mobility of an oil, since the more mobile a liquid the less difference will there be in the rapidity of its revolution in different parts of the vessel. Hence the product, Tv_0, is termed the " mobility."

If the mobility were entirely dependent on the coefficient of internal friction, the viscosity and mobility would be parallel in all liquids, which is not the case. The " mobility " decreases steadily with the rise in temperature, and, when the consistency exceeds 30 revolutions, fatty oils lose their oily character. The curves for the two values at different temperatures do not run parallel, and are of different grades in different liquids.

In the case of rape oil, the relation between the consistency, U, and the viscosity, V, can be expressed with approximate accuracy by the formula

$$(V + 1{\cdot}92)(U - 0{\cdot}08) = 387{\cdot}54,$$

and the following table gives the comparative results, as observed and calculated by this formula for that oil at different temperatures :—

Revolution in consistency apparatus,	17	20	24	28	30	40	56
Minutes (viscosimeter), . .	21·0	17·3	14·2	12·0	11·15	7·9	4·5
Tv_0, . . .	357·0	346·0	340·8	336·0	334·5	316·0	252·0
Minutes, calculated,	20·98	17·53	14·28	11·96	11·03	7·78	5·01

The curves of the changes in the viscosity and consistency are parallel to the curves of those brought about by heat.

The tables on p. 123 give, in an abridged form, some of the determinations made by *Weiss* in illustration of these points.

These substances thus stand in the following ascending order as regards " mobility " :—Soluble glass, glycerin, soap solutions, gum solutions, rape oil, melted lard, castor oil, liver oil, mineral oil. It is characteristic of castor oil that its " mobility " increases as it becomes more fluid.

Doolittle's Torsion Viscosimeter.[1]—In this instrument, which is particularly suitable for very heavy oils, the retarding effect of the liquid upon an oscillating torsion pendulum is measured. The results, which are independent of the specific gravity of the oil, thus indicate the extent to which the viscosity checks the swing of the pendulum.

Essentially the apparatus consists of a steel cylinder, 2 ins. by 1½ ins., suspended by means of a steel wire, which passes through and is attached to a graduated disc. The cylinder is filled with the oil and suspended in a vessel also containing the oil. The pendulum disc is turned to the zero point, where it is fixed by means of a thumb screw, and after the oil has been brought to the required temperature the disc is released, and two complete oscillations to the right and to the left are measured.

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[1] *J. Amer. Chem. Soc.*, 1893, xv., 173.

If, for example, neglecting the initial swing, the pendulum swings to 330 in one direction, then to 320 in the other, and back again to 312, the retardation will be :—

$$\begin{array}{rl} (1)\ 330 + 320 = & 652 \\ (2)\ 320 + 312 = & 630 \\ \hline \text{Retardation} = & 20 \end{array}$$

The instrument is standardised on a solution of pure cane sugar, and the results are numerically expressed in terms of the weight of sugar in grammes which in 100 c.c. of syrup (at 60° F.) will effect at 80° F. the same degree of retardation as the oil under examination.

Sheppard's Instrument.—This apparatus has been devised for determining the absolute viscosity of very viscous liquids. The method is based on the velocity of the fall of a smooth rigid sphere such as a polished steel ball, through the liquid. The absolute viscosity may be calculated by the application of Stokes's law—

$$\frac{K\,2g\,R^2\,(S - S^1)}{g\,V},$$

where K represents the coefficients of viscosity, V the observed velocity of fall, g the gravitational constant, S the density of the spherical body, S^1 that of the liquid, and R the radius of the sphere. Corrections based on experimental data must also be applied, since Stokes's law demands that the liquid shall be of infinite extent.[1]

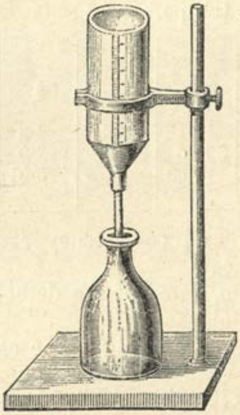
Fig. 21.—Schübler's Viscosimeter (Efflux Method).

Efflux Method.—The simplest arrangement for making comparisons between different oils, etc., as regards their efflux velocities, consists of an ordinary pipette filled up to a given mark on the stem with the oil to be tested, a note being taken of the time required for the oil to run out either completely, or down to some lower mark. Fig. 21 represents an instrument on this principle devised by *Schübler*, the upper part of the pipette being expanded into a reservoir, with a scale attached indicating the level to which the fluid sinks. For comparative observations, the reservoir is filled to a given level, and the time determined during which the level sinks to a given extent, (*a*) in the case of the substance tested, (*b*) in the case of some other substance taken as standard.

The time ratio thus deduced does not represent the relative time for *equal weights*, but that for *equal volumes ;* so that to obtain the ratio for equal weights the value $\frac{t_1}{t_2}$ must be multiplied by $\frac{d_2}{d_1}$, where d_1 is the relative density of the substance examined, and d_2 that of the

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[1] *J. Ind. Eng. Chem.*, 1917, ix., 523.

I.

Revolutions in Apparatus.	Glycerin, Specific Gravity 1·263 at 20° C.			Rape Oil.			Mineral Oil.			Liver Oil.			Castor Oil.		
	Minutes Viscosity.	Temperature.	Mobility.	Minutes Viscosity.	Temperature.	Mobility.	Minutes Viscosity.	Temperature.	Mobility.	Minutes Viscosity.	Temperature.	Mobility.	Minutes Viscosity.	Temperature.	Mobility.
		°C.			°C.			°C.			°C.			°C.	
14	19·0	17·4	266·0	...	...	...	20·6	26·6	288·4	...	...	...	...	...	...
18	14·65	21·4	263·7	19·7	9·0	354·6	15·6	30·3	280·8	...	...	...	16·4	51·3	295·2
24	10·8	26·0	259·2	14·2	16·2	340·8	12·1	34·8	290·4	12·4	7·9	297·6	12·3	57·0	295·2
26	10·0	27·0	260·0	13·0	18·2	338·0	11·2	36·0	291·2	11·5	9·5	299·0	11·6	58·4	301·6
36	6·6	34·0	237·6	9·0	25·6	324·0	7·6	42·8	273·8	7·8	17·7	280·8	...	...	...
48	4·15	43·4	199·2	6·2	35·4	297·6	5·0	50·4	260·0	5·5	27·5	264·0	...	...	...
56	2·45	54·0	137·2	4·5	45·0	252·0	...	...	...	4·0	37·0	224·0	...	...	...

II.

SUBSTANCE.	No. of Revolutions.	Viscosimeter Minutes.	Mobility.
Melted lard at 41·2° C.,	52	4·8	249·6
" " 47·2° C.,	56	3·9	218·4
Lubricating soap dissolved in water and spirit at different temperatures—			
a,	22·1	12·8	282·9
b,	24·1	10·15	244·6
Aqueous solution of gum arabic—			
a,	13·65	19·9	291·6
b,	59·6	6·4	453·4
Soluble glass,	35·5	5·6	198·8

standard substance. Thus, if the substances contrasted were sperm and rape oils, and the respective times necessary for the same volume to flow out were 40 and 120 seconds, whilst the relative densities were 0·880 and 0·915 respectively, the relative efflux rate for equal weights would be

$$\frac{t_1}{t_2} \times \frac{d_2}{d_1} = \frac{40 \times 0{\cdot}915}{120 \times 0{\cdot}880} = 0{\cdot}347.$$

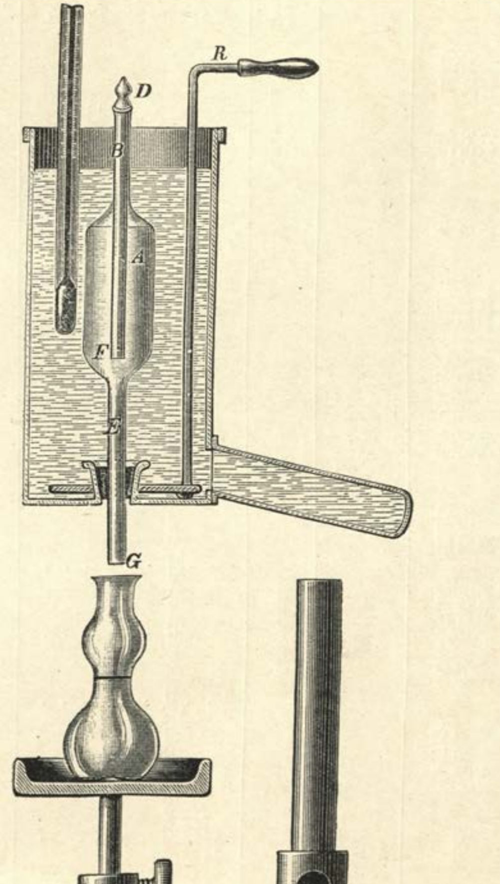

Fig 22 —Schmid's Viscosimeter.

As the time of efflux varies to a marked extent with the temperature (usually diminishing as the temperature rises), such comparisons must necessarily be made under constant conditions as to temperature.

Schmid - Reischauer Viscosimeter.—In order to ensure uniformity of temperature in different experiments the results of which are to be compared, the vessel containing the oil may conveniently be surrounded with a jacket containing water or a melted paraffin wax. Fig. 22 represents an arrangement of the kind described by *E. Schmid*, which also contains a device for maintaining a constant pressure during the outflow, instead of having a continually varying "head," as in Schübler's instrument. The vessel containing the oil, A, is a sort of pipette, excepting that the upper end consists of a tube, B, passing down inwards to a point, F, near the base of the expanded part. The upper end of B is closed by a stopper, D, so that when the stopper is in, no air can enter, and, consequently, no oil runs out at G; but on removing the stopper the oil flows out. The pipette, which contains some 50 c.c., is filled by removing the stopper, inverting the tube with the end B D immersed in the oil, and applying suction at the other end G. The stopper being replaced, the pipette is fixed in position inside the water jacket, which is heated to the required temperature in the ordinary way by means of the projecting tube. A stirrer, R, with an annular plate at the end is provided; by moving this up and down the temperature is equalised. When the required temperature is attained the stopper is withdrawn and the time ascertained which a given volume of oil requires to run out. As long as the level of the oil in the pipette does not fall below F, the pressure or "head" under which the oil issues at G is manifestly constant, being that due to a column of oil of length, G F. By employing high-boiling paraffin oils, etc., in the water jacket, the relative efflux times for various oils at high temperatures can thus be readily determined.

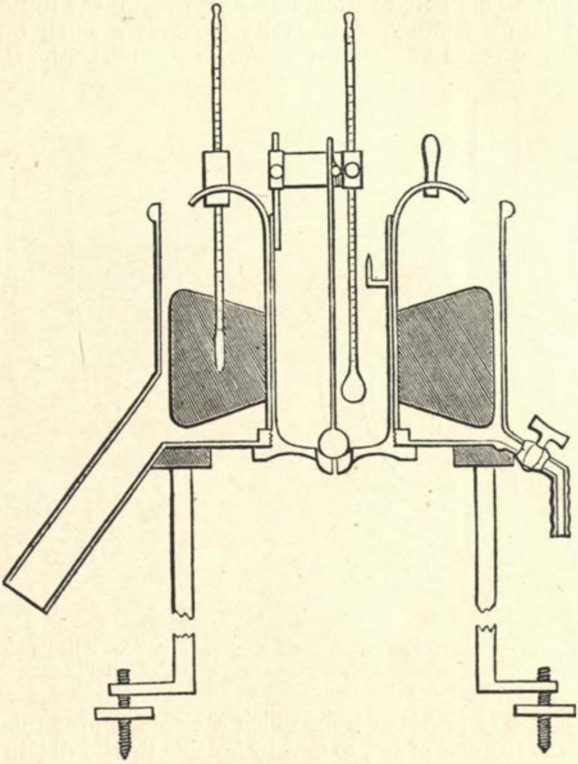

Fig. 23.—Redwood's Viscosimeter.

With all instruments of this description a variable amount of friction is brought into play as the oil passes through the efflux pipe, especially when this is conical; so that varying results are often obtained with different instruments. This source of error is best avoided by doing away with the efflux tube altogether, and substituting for it a hole drilled in a plate of glass or agate.

Redwood's Efflux Viscosimeter.—Figs. 23 and 24 represent Boverton Redwood's form of viscosimeter, consisting of an interior silvered copper cylinder, about 1½ ins. diameter and 3½ ins. deep, containing the oil to be examined. The bottom of this is furnished with an orifice, consisting of a hole bored through an agate plate, the top of which is excavated into a hemispherical cavity, so that a small brass sphere attached to a rod and dropped in forms a sufficiently tight valve.

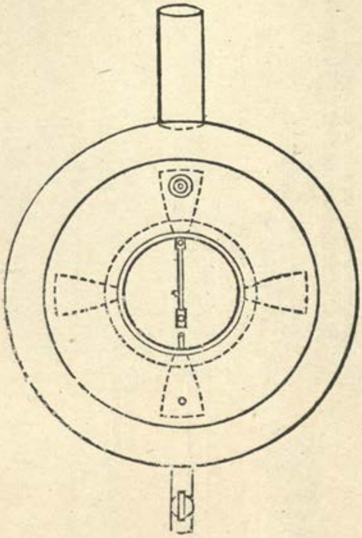

Fig. 24.—Redwood's Viscosimeter.

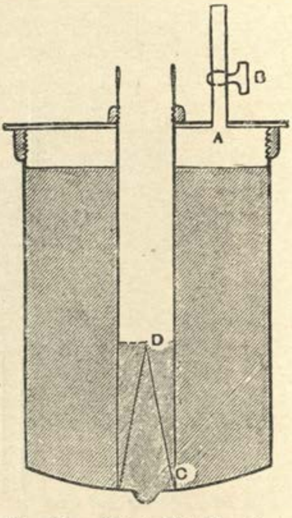

Fig. 25.—Allen's Modification of Viscosimeter.

An outer jacket is provided from which a closed copper tube projects downwards at an angle of 45°, so that by heating this "tail" in a Bunsen or spirit lamp flame, the temperature of the liquid (water, oil, melted paraffin wax, etc.) in the jacket can be raised as required. A revolving agitator to equalise temperature in the jacket is provided, with a thermometer attached, a second thermometer being supported in the oil by a clamp fixed to the cylinder. The whole rests on a tripod stand furnished with levelling screws. The constancy of initial level of oil inside the cylinder is assured by means of a gauge consisting of a small internal bracket with upturned point.

When an observation is to be made, the bath is filled with water, or heavy mineral oil, etc., and heated to the required temperature.

The oil to be tested is also heated to this temperature and poured in until the level of the liquid just reaches the point of the gauge. A narrow-necked flask, holding 50 c.c., is placed beneath the jet immersed in a liquid at the same temperature as the oil. When all is ready the ball-valve is raised and a stop-watch started, and the number of seconds requisite to fill the 50-c.c. flask noted, care being taken that the temperature does not fluctuate during the time, and that the oil is perfectly free from suspended matter, such as dirt or globules of water.

Allen's Modification.—In order to obviate the necessity of always using the same volume of oil (indispensable in order to end with the same difference of level, and consequently maintain the same average head or pressure throughout), *Allen*[1] makes an addition consisting of an air-tight cover, Fig. 25, perforated by two holes, one of which, A, is furnished with a tap, B, while the other has another tube screwing air-tight into it. This tube, C, is prolonged on two sides in contact with the agate orifice, whilst the angles of the inverted V-shaped slits cut on each side terminate at D, exactly 1½ inches higher. The cylinder is completely filled with oil before commencing an observation, the tap, B closed, and the orifice opened till the oil sinks to the level of

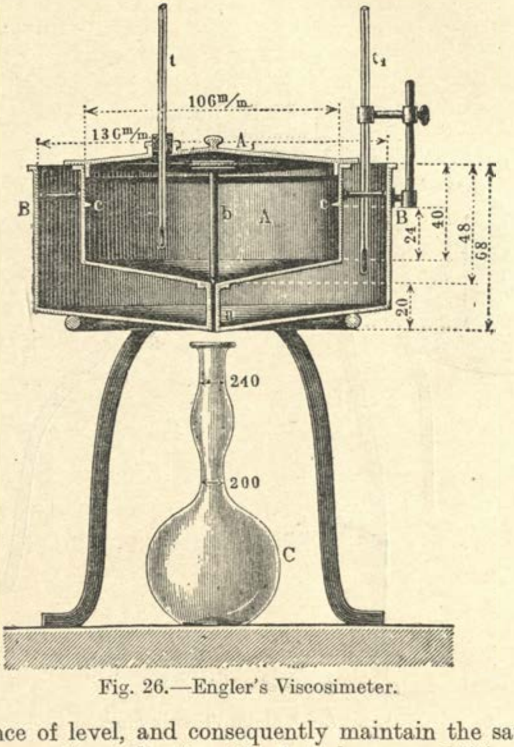

Fig. 26.—Engler's Viscosimeter.

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[1] *J. Soc. Chem. Ind.*, 1886, v., 131.

D in the inner tube. Air then bubbles regularly in at D; when this happens, the temperature is noted and the oil collected in a graduated receiver. Any volume from 10 to 50 c.c. can thus be run out, as the oil falls in the upper part of the cylinder, but is maintained constantly at the level, D, in the inner tube. Five consecutive valuations of 10 c.c. each may thus be made, while 50 c.c. run out.

An apparatus has been devised by Cope,[1] in which, to obviate the effect of variations in the pressure due to the height of the column of liquid over the orifice, the liquid is driven at a definite temperature through the opening by means of measured centrifugal force, and the viscosity is expressed in terms of the acceleration due to gravity.

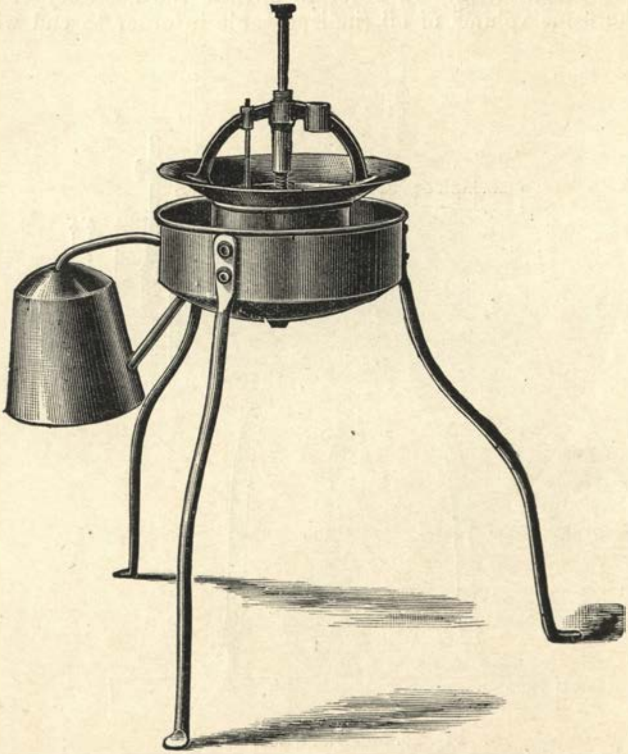

Fig. 27.—Hurst's Viscosimeter.

Several other forms of viscosimeter have been constructed by other chemists, based on the efflux principle. Fig. 26 represents in section Engler's instrument. A slightly modified form of this by *Engler* and

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[1] *J. Ind. Eng. Chem.*, 1917, ix., 1046.

Künkler[1] is largely used on the continent.[2] Fig. 27 represents a simple form constructed by *G. H. Hurst.*[3] The oil, etc., to be examined is run into the innermost vessel up to a given height determined by a gauge-pin, and heated up to the required extent by applying a Bunsen burner or spirit lamp to the heater at the side, connected by two tubes with the water reservoir surrounding the oil chamber, so as to heat the water by circulation. The temperature of the oil is taken by means of a thermometer (usually this registers about 6° F. below the temperature of the water in the jacket); and when the required temperature is reached, the central valve is raised and 50 c.c. of oil allowed to run out into a measuring flask underneath, the time of efflux being noted. Obviously, with this instrument, the head under which the liquid issues is continually diminishing as it flows.

From a comparative examination of the results obtained by means of Engler's, Redwood's, and Saybolt's viscosimeters, *Meissner*[4] has found that the efflux period, t_r, measured by Redwood's viscosimeter, and t_s by Saybolt's universal viscosimeter, may be reduced to Engler degrees, E, by means of the following formulæ :—

$$t_r = 192{\cdot}2\,k\,(1 + \sqrt{1 + \frac{0{\cdot}01624}{k_2}}$$

$$t_s = 228{\cdot}7\,k\,(1 + \sqrt{1 + \frac{0{\cdot}01309}{k_2}}$$

$$k = 0{\cdot}08019\,\mathrm{E} - 0{\cdot}07613\,1/\mathrm{E}.$$

The values thus calculated agreed within 4 per cent. of those observed with Redwood's apparatus, and within 2 per cent. in the case of Saybolt's apparatus.

Higgins[5] found that in the case of Redwood's instrument the following formula gave results agreeing within 5 per cent. of the true viscosity, η :—

$$\eta = \left(0{\cdot}0026\,\mathrm{T} - \frac{1{\cdot}715}{\mathrm{T}}\right)\delta,$$

where T represents the efflux velocity in seconds and δ the density of the liquid at $t°$ C.

In the case of Engler's viscosimeter a corresponding formula has been worked out by *Ubbelohde*[6] :—

$$\eta = \left(0{\cdot}001435\,\mathrm{T} - \frac{3{\cdot}22}{\mathrm{T}}\right)\delta.$$

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[1] *J. Soc. Chem. Ind.*, 1890, ix., 654 ; from *Dingler's polyt. J.*, cclxxvi., 42.

[2] A more recent form is described by Engler, with special instructions for its use (*J. Soc. Chem. Ind.*, 1893, xii., 291 ; from *Zeit. angew. Chem.*, 1892, 725).

[3] *J. Soc. Chem. Ind.*, 1892, xi., 418.

[4] *Chem. Rev. Fett Ind.*, 1912, xix., 30.

[5] *J. Soc. Chem. Ind.*, 1913, xxxii., 568

[6] *Tabellen zum Englerschen Viskosimeter*, 1907.

Standards of Efflux Viscosity.—In actual practice, water is too fluid to be a convenient standard substance; *rape oil* is usually chosen in preference, because, notwithstanding the unavoidable differences that exist between samples from seeds grown in different countries and soils, these differences are usually not extremely wide. Definite mixtures of pure glycerol and water, however, can be readily prepared, possessing almost any required higher degree of "viscosity,"[1] and capable of use as standards of comparison of considerably greater uniformity, when prepared by different operators at different times, than is possible with natural products such as rape oil.

In the subjoined table of results obtained by *Crossley* and *Le Sueur*[2] are given the velocity of efflux of different Indian oils compared with water at the same temperature. These values were determined in a Redwood's viscosimeter.

Oil or Fat.	Seconds for flow of 50 c.c. at 70° F.	Compared with water at 70° F.	Oil or Fat.	Seconds for flow of 50 c.c. at 70° F.	Compare with water at 70° F.
Evergreen tree, .	375·8	14·79	Radish-seed, .	385·3	15·17
Earth-nut, . .	350·1	13·78	*Eruca Sativa*, .	371·0	14·61
Mexican poppy, .	429·3	16·90			
Rape-seed, . .	390·6	15·38			
White mustard, .	402·0	15·82	Solid Fats.	At 140° F.	At 140° F.
Black mustard, .	425·4	16·75			
Safflower, . .	256·1	10·08			
Niger-seed, . .	292·6	11·52	Bassia butter, .	97·1	4·24
Walnut, . .	231·8	9·13	Indian butter, .	110·4	4·82
Garden cress, .	321·6	12·66	(*Bassia butyriacea*)		
Linseed, . .	211·7	8·33	Coconut oil, .	63·9	2·79
Olive, . . .	312·3	12·29	Kokam butter, .	101·1	4·41
Poppy, . .	254·8	10·03	White Dammar, . (Piney tallow)	104·0	4·54

The following tables are selected from the numerous results published by various authorities, as illustrating the general character of the numbers obtained with "viscosimeters" of different kinds for determining the relative efflux rates of different natural oils, etc., and lubricants made therefrom, or from petroleum and other hydrocarbons, and the effect of variations of temperature on the values. The figures obtained by *Schübler* represent the "viscosity degree" (*Viscositätsgrad*)

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[1] With the viscosimeter above described, Boverton Redwood finds that the relative times requisite for 50 c.c. of water and genuine rape oil to flow out at the temperature of 15·5° C. (60° F.) are 25·5 and 535 seconds respectively, taking the average of various samples of pure oil. Allen finds that glycerol, diluted with water until the specific gravity at 15·5° C. is 1·226, possesses the same degree of viscosity as average rape oil when tested in the same way.

[2] *J. Soc. Chem. Ind.*, 1898, xvii., 992.

or "relative viscosity" of the respective oils—*i.e.*, the relative times requisite for *equal volumes* to pass (at 7·5° and 15° C. respectively), the times required by the same volume of water being taken as unity. Those quoted from the other authorities are not thus reduced, but are simply the actual times directly observed with the particular instruments used :—

Name of Oil.	Relative Time in Seconds (*Schübler*).		
	Plant from which derived.	At 7·5° C.	At 15·0° C.
Castor,	Ricinus communis,	377·0	203·0
Olive,	Olea europæa,	31·5	21·6
Hazel-nut,	Corylus avellana,	24·2	18·4
Colza,	Brassica campestris oleïfera,	22·4	18·0
Rape,	Brassica rapa oleifera biennis,	22·6	17·6
Beech-nut,	Fagus sylvatica,	26·3	17·5
White mustard,	Sinapis alba,	24·0	17·4
Almond,	Amygdalus communis,	23·3	16·6
Spindle-nut,	Euonymus europæus,	23·3	15·9
Black mustard-seed,	Sinapis nigra,	19·4	15·6
Poppy-seed,	Papaver somniferum,	18·3	13·6
Cameline-seed,	Myagrum sativum,	17·7	13·2
Belladonna-seed,	Atropa belladonna,	17·3	13·1
Sunflower,	Helianthus annuus,	16·4	12·6
Turpentine,	Pinus sylvestris,	16·7	11·8
Cress,	Lepidium sativum,	14·4	11·4
Grape-seed,	Vitis vinifera,	14·2	11·0
Plum-kernel,	Prunus domestica,	14·7	10·3
Tobacco-seed,	Nicotiana tabacum,	13·5	10·0
Walnut,	Juglans regia,	11·8	9·7
Linseed,	Linum usitatissimum,	11·5	9·7
Hemp-seed,	Cannabis sativa,	11·9	9·6

Oils, &c., Used.	Relative Time in Seconds (*Wilson*).		
	At 15·5° C. = 60° F.	At 49° C. = 120° F.	At 82° C. = 180° F.
Sperm oil,	47	30·5	25·75
Olive oil,	92	37·75	28·25
Lard oil,	96	38	28·5
Rape oil,	108	41·25	30
Neat's foot oil,	112	40·25	29·25
Tallow oil,	143	37	25
Engine tallow,	Solid.	41	26·5

Redwood's results are indicated graphically by the curves indicated in Figs. 28 and 29.

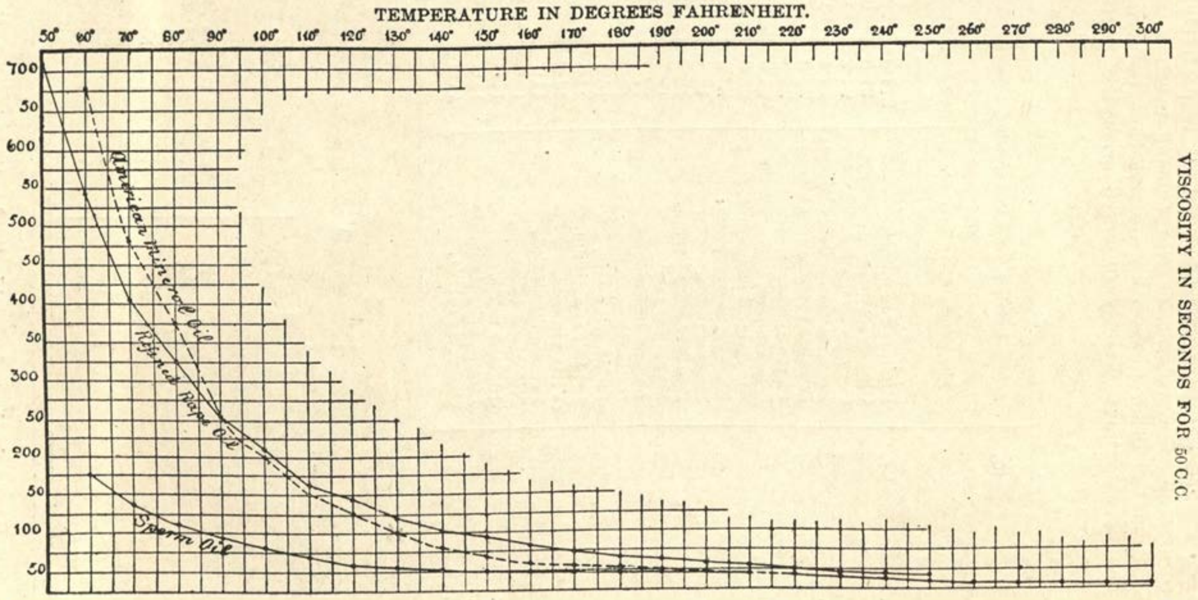
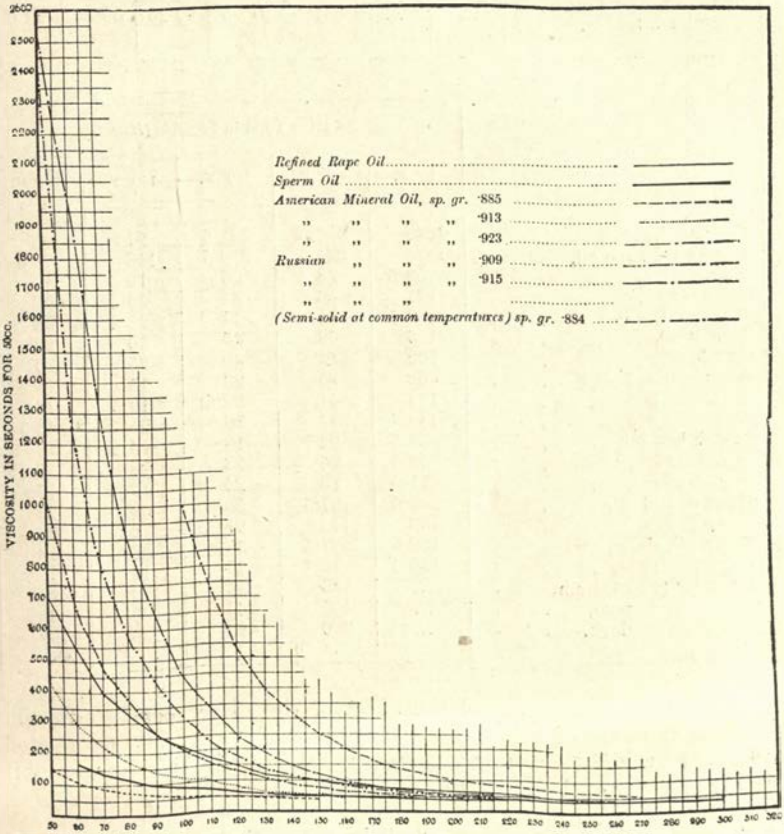


Fig. 28.—Redwood's Chart of Viscosity of Oils.

Oils Employed.	Relative Time in Seconds (*Allen*).			
	Spec. Grav. at 15·5° C.	At 15·5° C. = 60° F.	At 50° C. = 122° F.	At 100° C. = 212° F.
Sperm oil, ...	·881	80	47	38
Seal oil (pale), . .	·924	131	56	43
Northern whale oil, .	·931	186	65	46
Menhaden oil, . .	·932	172	40	..
Sesamé oil, ...	·921	168	65	50
Arachis oil, ...	·922	180	64	...
Cotton-seed oil (refined),	·925	180	62	40
Niger-seed oil, . .	·927	176	59	43
Olive oil, ...	·916	187	62	43
Rape oil, ...	·915	261	80	45
Castor oil, ...	·965	2420	330	60



Temperature in Degrees Fahrenheit.

Fig. 29.—Redwood's Chart of Viscosity of Oils.

	Relative Time in Seconds (*Redwood*).						
	50° F.	70° F.	100° F.	140° F.	200° F.	250° F.	300° F.
Refined rape oil, No. 1,	712·5	405	147	105·5	58·5	43·25	...
,, ,, ,, 2,	...	406	146	106·5	57·5	...	...
,, ,, ,, 3,	..	405·5	147	106·5	57·5	...	...
,, ,, ,, 4,	...	407	147·5	106	58·5	...	...
Beef tallow, . . .	...	...	...	...	54·75	40	...
Sperm oil, . . .	...	136 8	60·5	50·75	42	34·75	30
Neat's foot oil, . .	620	366	126	88·4	50·4	44	38
American mineral oil, specific gravity ·885,	145	90	47	41	...	...	...
American mineral oil, specific gravity ·923,	1030	485	126	82	42	...	...
Russian mineral oil, specific gravity ·909,	2040	820	174	116	48·5	...	...
Russian mineral oil, semi-solid, . .	...	...	531	317·5	99·25	59·25	42·6

	Relative Time in Seconds (*Hurst*).				
	70° F.	100° F.	120° F.	150° F.	180° F.
Castor oil, ...	1248	487·5	201·5	91	48
Thickened rape oil, . .	1370	331·5	279·5	156	78·5
Sperm oil, ...	58·5	36·4	26	19·5	17
Colza oil, ...	131	56	44	32·5	28
Whale oil, ...	128·7	61	44	28·5	28
Tallow oil, ...	105	63	45	30	20
Cotton oil, ...	100	55	40	25	20
American 885 oil, . .	68	35	23	15	14
,, 905 ,, . .	113	44	32·5	19·5	18
,, 915 ,, . .	140	47	36	21	19·5
Scotch 865 oil, . . .	32·5	22	18	15·5	13
,, 885 ,, ...	58·5	26	22	18	15·5
,, 890 ,, ...	71·5	39	26	19·5	17
Russian 906 oil, . . .	292·5	97·5	56	30	22
,, 911 ,, ...	462	143	91	82·5	26
Rosin oil, dark, . . .	152·5	97·5	38	22	18
,, pale, ...	136·5	49·4	25	18	17
Cylinder oil, medium, .	...	385	255	170	70
,, pale, . .	...	405	265	120	90
,, dark, . .	...	890	495	230	100

As further illustration of the effect of rise of temperature in diminishing the rate of efflux, the following figures may also be quoted, obtained by *Villavecchia* and *Fabris*, whilst investigating certain lubricating oils [1] for excise purposes :—

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[1] *Report of the Central Laboratory of the Italian Customs Department*, 1891 ; also *J. Soc. Chem. Ind.*, 1891, x., 390.

Lubricating Oil.	Efflux Rate referred to Water at	
	20° C.	50° C.
No. 1	44·39	6·31
,, 2	51·07	5·94
,, 3	40·85	5·50
,, 4	38·77	6·03
,, 5	72·09	8·35
,, 6	67·92	9·66
,, 7	56·03	5·71

Thus, the effect of a rise in temperature from 20° to 50° C. is to diminish the efflux rate to $\frac{1}{6} - \frac{1}{10}$ of the original value, the effect being more marked with the more viscous fluids.

According to experiments by *Bender*,[1] when an oil is chilled to — 20° for some time, and then warmed up again, the efflux viscosity value at the ordinary temperature is often considerably increased as compared with what it was previously at the same temperature of observation, thick oils usually showing a greater increment than thinner ones. On the other hand, if oils are heated up to 50° or 100°, and then allowed to cool down again to the air temperature, the thicker oils become perceptibly thinner, whilst the thinner oils are less affected.

The "Mercurial Viscosimeter."—An instrument has been devised by *Lidstone*[2] for the examination of minute quantities of oil, for which the ordinary standard instruments are quite unsuitable. It consists essentially of a capillary tube in the middle of which is blown a small bulb. The tube has a stop-cock at the base and a receiving cap at the top, and is surrounded by a water-jacket at the required temperature. The tube is filled with mercury, and the oil is introduced into the cap so that it rests on the mercury, and is brought to the definite temperature. The tap is then opened, and the time taken by the mercury in falling from a point above to a point below the capillary bulb is recorded. The efflux velocity may be converted into Redwood degrees by means of the formula—

$$R = \frac{t}{d}k,$$

where t represents the observed time, d the density of the oil at the definite temperature, and k a constant which may be found by parallel determinations in this and Redwood's instrument. In a modified form of this instrument intended for volatile liquids an equal excess pressure is produced, by means of an attachment, above and below the liquid.[3]

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[1] *J. Soc. Chem. Ind.*, 1891, x., 936; from *Mitth. a. d. Königl. techn. Versuchsamt.*, Berlin, 1891, 100.

[2] *J. Soc. Chem. Ind.*, 1917, xxxvi., 270.

[3] *Ibid.*, 1918, xxxvii., 148 T.

Relation between Viscosity and Iodine Value.—*Crossley* and *Le Sueur*[1] have pointed out that there is apparently a close connection between the viscosity and the iodine value. This may be attributed to the fact that, speaking generally, the more unsaturated the oil, the greater the percentage of the more unsaturated fatty acids present, and these, as is well known, do not solidify readily when cooled.

The following comparative results illustrate this point:—

Oil.	Iodine Value.	Viscosity at 21° C.	
		No. of Seconds.	Compared with Water.
Earth-nut, . .	92·43	429·3	16·90
,, . .	98·42	347·0	13·67
Mexican poppy, .	119·9	272·0	10·71
,, .	122·53	268·9	10·59
Rape-seed, . .	94·10	464·6	18·29
,, . .	96·25	393·2	15·48
,, . .	104·84	371·8	14·64

Viscosity of Soap Solutions.—*Blasdale*[2] recommends a method in which the oil is first saponified and the viscosity of the soap solution determined after being diluted to a definite volume:—15 grammes of the oil are saponified on the water-bath with exactly 7·5 grammes of potassium hydroxide and 10 c.c. of alcohol. The soap solution is heated to expel the alcohol, then diluted to 200 c.c., and examined in the viscosimeter. The viscosity is expressed in terms of grammes of sugar, which it would be necessary to add to a litre of water to obtain an equal value. In this way the following results were obtained:—

Oil.	Viscosity in Grammes of Sugar per Litre of Water.
Cotton-seed, ...	280
Almond, ...	645
Rape, ...	670
Poppy, ...	95
Earth-nut, ...	220
Lard, ...	250
Sesamé, ...	415
Acorn, ...	305
Pine-nut, ...	100
Californian nutmeg, . .	235

Lepenau's Leptometer.—This instrument is based on a principle somewhat different from that involved in the above described forms of efflux viscosimeter, inasmuch as it depends not only on the rate of flow through a given orifice, but also on the amount of surface tension

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[1] *J. Soc. Chem. Ind.*, 1898, xvii., 990.

[2] *J. Amer. Chem. Soc.*, 1895, xvii., 935.

called into play when drops are formed in air. It consists essentially of a pair of precisely similar cylinders, B B (Fig. 30), immersed in the same bath, A, one of which contains the oil to be examined, and the other another oil used as a standard of comparison; the relative rate at which drops form as the oil passes through equal sized capillary tubes, *r*, *r*, the dimensions of which are too small to permit of continuous streams being produced, the quantities flowing out in a given time being weighed or measured.

All these various forms of instrument are subject to one constant source of error—viz., that the forces coming into play when the viscous liquid passes through a tube or orifice under given conditions to temperature, etc., are not the same as those obtaining when the liquid is used as a lubricant for shafting, quickly rotating spindles, axles, and the like; and, consequently, that the figures obtained by means of such testing appliances are only approximations (and not always close ones) to the relative values of the substances examined, when practically applied for lubricating purposes.

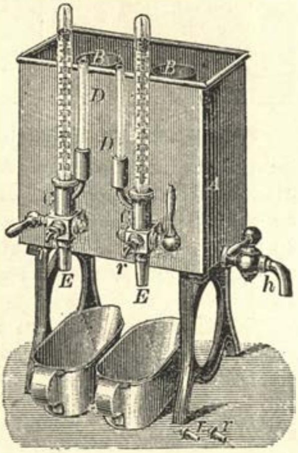

Fig. 30.—Lepenau's Leptometer.

Determination of Viscosity in Absolute Measure.—When liquids are examined possessing a comparatively low degree of viscous character, the rate of flow through a narrow orifice does not represent the true physical "viscosity," because a large proportion of the result is due to flow pure and simple without any "shear." Accordingly, when a comparatively long, narrow, accurately calibrated tube is made use of as the jet, figures are obtained not always showing close agreement with those yielded by the ordinary forms of efflux apparatus. According to mathematical investigations by Poiseuille and others, the coefficient of friction in narrow tubes is given by the formula

$$\eta = \frac{\pi p r^4 t}{svl},$$

where η is the coefficient of friction, t the time of efflux, v the volume of fluid discharged, p the hydraulic pressure, l the length and r the radius of the capillary tube, and s the specific gravity of the liquid.[1] Starting from this, *E. J. Mills* has made some measurements in absolute measure of the coefficients of friction for various liquids, including water, and sperm, olive, lard, and castor oils.[2]

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[1] Hagenbach arrives at a formula involving a second term in addition to that given by Poiseuille—

$$\eta = \frac{\pi p r^4 t}{svl} - \frac{vs}{2\frac{10}{3}\pi lt}.$$

[2] *J. Soc. Chem. Ind.*, 1886, v., 148; also, 1887, vi., 414.

On the C.G.S. system (centimetre, gramme, and second as units of length, mass, and time respectively) Poiseuille's formula becomes

$$= \frac{\pi p r^4 t}{svl} \times 98 \cdot 1,$$

where v is given in cubic millimetres, and r, l, and p in millimetres. From this formula and his experimental results, Mills deduces the following values at 12° C. :—

	Specific Gravity.	Value of η.	Relative Viscosity, Water = 1.
Water, . . .	1·000	0·011713	1·00
Sperm oil, . .	0·88789	0·68828	58·76
Olive oil, . .	0·92043	1·1393	97·27
Lard oil, . .	0·92051	1·6285	139·03
Castor oil, . .	0·96541	21·721	1,854·4

Obviously these relative vicsosity values are very dissimilar from Schübler's numbers for castor and olive oils compared with water, although the ratios between the values for the oils alone do nor differ so widely in the two cases. This chiefly arises from the error attaching to the viscosity determination in the case of water by the efflux method through a jet, as compared with the true value through a long narrow tube.[1]

Coefficient of Friction in Capillary Tubes.—*Traube* has constructed an arrangement of determining with considerable accuracy and speed the friction coefficients for oils and other liquids passing through capillary tubes under pressure. Fig. 31 represents this apparatus.[2] A is a Marriotte bottle filled with water, which serves to compress air in the reservoir, B, and to keep the pressure constant. B is connected by means of a pipe and cock to the efflux apparatus, H, consisting of the bulb, G (provided with two marks to permit the measurement of volume of liquid to be discharged), and the capillary tube, F. The reservoir, B, is filled by means of a pump attached to branch and stop-cock. When the observations are to be made at temperatures above that of the atmosphere a suitable air-bath is employed. When cleaning is required, ether is forced through the tube. With tubes of different diameters, the relative times observed for water and oils of high viscosities are not identical ; but for oils of considerable viscosity the differences are not great. Thus the following figures were observed with a cylinder lubricating oil and with olive oil as compared with rape-seed oil, being the respective times of efflux in seconds :—

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[1] The determinations of absolute " viscosity " values of solutions of gum relatively to water made by noting the times required for given volumes to pass through a known capillary tube, show similar differences when compared with the corresponding values obtained with a " jet " apparatus, such as a burette (*vide* paper by Rideal, *J. Soc. Chem. Ind.*, 1891, x., 610).

[2] *J. Soc. Chem. Ind.*, 1887, vi., 414.

Diameter of tube in millimetres, . .	1·5	0·8	0·5
Cylinder oil, . .	155·5 = 100·0	472 = 100·0	2,960 = 100·0
Rape-seed oil, . .	79·0 = 50·8	242 = 51·3	1,503 = 50·8
Olive oil, . .	71·7 = 46·1	222 = 47·0	1,364 = 46·1

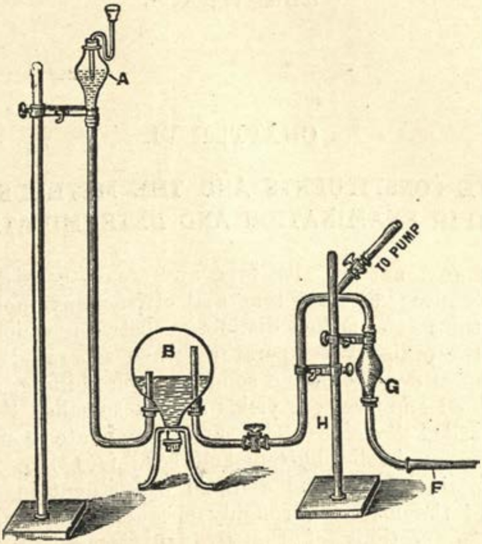

Fig. 31.—Traube's Apparatus.

In all probability the conditions existing when oil is forced through a capillary tube are more nearly akin to those obtaining with a film of oil lying between a shaft and its journal box than are those which are present in the ordinary form of efflux viscosimeter. Hence it is probable that the results of determinations on Traube's system would be valuable as yielding results more closely approximating to the actual practical lubricating values. Traube's apparatus, however, is far less convenient for ordinary laboratory work than Redwood's or Engler's viscosimeter.

§ 3. Chemical Properties of Oils, Fats, Butters, and Waxes.

CHAPTER VI.

PROXIMATE CONSTITUENTS AND THE METHODS USED FOR THEIR EXAMINATION AND DETERMINATION.

VERY few, if any, natural oils, fats, and waxes consist of one single chemical substance; at least two, and often many more constituents are present, the most marked distinction between which is that some are solid at the ordinary temperature (when separated), others liquid. The former often deposit in the solid form on chilling, so that a fluid oil, when chilled and pressed, yields a solid so-called "stearine" and a liquid so-called "oleine"[1] as first proximate constituents. In similar fashion semi-solid butters and hard fats, like tallow, can be shown to contain a solid and a liquid constituent in each case, the consistency of the material, roughly speaking, depending simply on the relative proportions of the two substances. When "oleine" largely predominates the substance is an oil; when "stearine," a hard fat; and when the two are in intermediate proportions, a more

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[1] The terms "stearine" and "oleine" are practically employed in several different senses, a circumstance apt to lead to considerable confusion. In the strict chemical sense, stearin is the glyceride of stearic acid, $C_3H_5(O.C_{18}H_{35}O)_3$, and olein the glyceride of oleic acid, $C_3H_5(O.C_{18}H_{33}O)_3$; but in the oil trade, generally, the two terms are applied to indicate respectively the solid and liquid constituents into which a fat or chilled oil can be mechanically separated, irrespective of the actual chemical composition of these constituents; whilst in the candle manufacture they are used to denote the analogous solid and liquid fatty acids obtainable from fatty matters by saponification and mechanical pressure, etc. Similar mixtures of free fatty acids and other substances are also obtainable by subjecting to distillation various kinds of grease (*e.g.*, Yorkshire grease—Chap. XII.). When these are chilled and pressed they are separated into solid and liquid portions, generally designated as "distilled" stearine and oleine respectively. In the present work the pure chemical triglycerides are distinguished by the terminal "in" (*e.g.*, *stearin*, *olein*, etc.); whilst the commercial articles are indicated by names ending in "ine" (*e.g.*, "*distilled*" *oleine*, candlemakers' *stearine*, *oleomargarine*, etc.). In similar fashion, the pure chemical compound $C_3H_5(OH)_3$ is referred to as "glycerol," whilst the commercial products mainly consisting of this body, but in a varying state of purity, are distinguished as *glycerin*.

or less buttery consistence is possessed at the ordinary temperature (near 15° C.).

The further investigation of the solid and liquid constituents thus obtainable from a given oil or fat; of the variations in their relative proportions and natures according to the soil and climate and other conditions under which the plant was grown in the case of vegetable oils or butter, or the species and habitat of the animal in that of an animal oil or fat; of the effect of cultivation and domestication, and various similar points, have, until recently, received but little attention. There appears, however, to be no doubt but that considerable differences in the relative amounts and even in the chemical nature of the various constituents of a given oil, etc., may, at any rate in some cases, be brought about by such causes. Thus, very different results have been obtained at various times in the examination of different samples of the kind of oil—*e.g.*, in the case of arachis oil (earth-nut oil), in which some observers have found more or less considerable amounts of *palmitic acid*, and others none at all.

Similar discrepancies in the results obtained by different investigators have been noticed in several other instances, thus leading to the conclusion that marked differences are apt to exist in the nature of oils and fats prepared from seeds, etc., grown under different conditions, just as is well known to be the case with fruits and other vegetable produce, as regards their saccharine matter and other constituents. Even without taking into account these natural variations, however, the knowledge at present extant of the proximate constituents of many of the more commonly occurring oily and fatty matters is decidedly scanty; whilst a very large number of similar substances exists (in many cases of great local importance, although not always materials largely exported or imported or otherwise dealt with commercially) concerning the general composition of which accurate knowledge is hitherto entirely wanting. Many such products promise in the near future to be important articles of trade, as soon as their respective values for particular purposes are better ascertained, and the best means to be adopted of extracting and refining them so as to render them marketable. In Central and Southern Africa, and in many other parts of the world, the progress of civilisation is continually tending to bring into notice new products of this kind, many of which only require attention being called to them to demonstrate their commercial value.

Much still remains to be done in the case of a considerable number of vegetable oils in the way of identifying and quantitatively estimating their various proximate constituents; and much the same remarks apply to certain animal oils, more especially "train oils" from marine cetaceans, as regards not only the acids present but also the alcoholiform constituents. Whilst it is known that certain of these oils are mainly composed of compound esters of non-glyceridic character, which furnish on saponification acids mostly of the oleic family, and as complementary products, alcohols of moderately high molecular weight, the complete investigation of the products thus formed has been attempted in but few instances. It appears, however, that besides alcohols of the ethylic series, others of a non-saturated character are also present in some of these oils, as the alcoholiform constituents extracted are in many cases capable of combining with iodine, leading to the conclusion that higher acrylic alcohols are also contained as compound esters in addition to cetylic alcohol homologues.

Separation of Glycerides.

The separation from one another of the different glycerides, etc., contained in a given " stearine " or " oleine " is, in most cases, a very difficult problem, more especially if required to be performed in such a fashion as to give an approximate idea of the relative proportions in which they are present.

Crystallisation from Ether.—Heintz showed many years ago that even after repeated crystallisations it is not possible to effect a complete separation of the glycerides of palmitic and stearic acid, and his results receive confirmation from the experiments of *Hehner* and *Mitchell.*[1]

In these experiments 140 grammes of a flare lard with an iodine value of 57·5, and the fatty acids of which contained 16·1 per cent. of stearic acid, were dissolved in a litre of hot ether. The fatty acids obtained from the crystals contained 32·4 per cent. of stearic acid, and those from the residue left on evaporation of the ether 15 per cent.

The main crop of crystals was recrystallised, and yielded crystals with fatty acids containing 47·6 per cent. of stearic acid, as against 17·23 per cent. in the fatty acids in solution. The second batch of crystals was once more recrystallised, with the result that the fatty acids in the crystals had now risen to 59 per cent., whilst the fat in solution contained 33·2 per cent.

It has been shown by *Bömer* that the stearic acid in lard (*q.v.*) is mainly present in the form of a mixed glyceride, and to this cause must be attributed the fact that only a small quantity of tristearin can be separated.

Seidenberg[2] has devised a method of fractionating glycerides, in which the fat is dissolved in two or more solutions, such as alcohol and ether, one of which is more volatile and has a greater solvent action than the other. Then by aspirating air through the solution gradual evaporation accompanied by a considerable reduction of temperature takes place, and the glycerides may be successively removed as they separate in the order of their insolubility. Similar fractions are combined and subjected to further fractionation. By this means, the mixed glycerides, oleodistearin, and dioleopalmitin have been isolated from tallow. The method is also applicable to the detection of beef and mutton fat in butter, the latter yielding a much smaller amount of insoluble glycerides than butter fat containing 20 per cent. of tallow.

Examination of Fatty Acids.—As a rule, the best results are obtained by saponifying the mixture, and applying methods for the

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[1] *Analyst*, 1896, xxi., 329.

[2] *J. Ind. Eng. Chem.*, 1917, ix., 855 ; 1918, x., 627.

separation of the resulting fatty acids, either by mechanical means (chilling and pressing out the more liquid portions) or by chemical processes (fractional precipitation, etc., *vide infra*).

Some oils and fats contain appreciable quantities of the glycerides of acids sufficiently low molecular weight to be volatile in a current of steam at the ordinary atmospheric pressure (*vide infra*).

Precipitation with Bromine.—*Hehner* and *Mitchell* have shown that certain oils yield insoluble compounds of glycerides with bromine (*cf. Mixed Glycerides* and *Linseed Oil*).

Alcoholysis of Glycerides.—A method of separating glycerides has been based upon their decomposition, with the formation of esters which can be separated by distillation. For this purpose the fat or oil is heated with an alcohol, such as methyl or ethyl alcohol, in the presence of an acid, when the fatty acids present are converted into the esters of the alcohol. On treating the alcoholic solution with an excess of water or of salt solution the esters are separated, and their composition may be determined by fractional distillation under reduced pressure.

The method has been shown by *Haller*[1] to be capable of determining the approximate composition of a fat, and was used by *Haller* and *Youssoufian*[2] in the examination of coconut oil, and by *Mayer*[3] to determine the nature of the fatty acids in cotton-seed oil.

From a critical examination of the method, however, *Elsdon*[4] concludes that although it may sometimes be useful in affording information as to the approximate composition of an oil or fat, it is too slow for ordinary laboratory purposes, and does not give quantitative results (see *Coconut* and *Palm kernel Oils*).

METHODS OF SEPARATING INDIVIDUAL FATTY ACIDS.

VOLATILE FATTY ACIDS.

Fractional Distillation and Precipitation.—After saponification and acidification, an acid distillate is obtainable by boiling, preferably by blowing a current of steam from a suitable generator through the mass. The slightly acid aqueous fluid may then be neutralised with an alkali, evaporated to a small bulk, and decomposed by a mineral acid; or converted into silver or barium salts, etc., and further examined.

If more than one volatile acid be present, a separation may often be effected by fractional precipitation as silver salt, etc.; or enough mineral acid may be added to liberate a fraction of the total organic acids from the evaporated solution of alkaline salts, and the distillation repeated; the acid of lowest molecular weight will then pass over. By similarly liberating successive fractions and distilling alternately, a series of distillates will be obtained, the acids of higher molecular weight being contained in the respective later fractions (*Liebig*).

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[1] *Comptes Rendus*, 1906, clxxiii., 657.

[2] *Ibid.*, 803.

[3] *Chem. Zeit.*, 1907, xxxi., 793.

[4] *Analyst*, 1913, xxxix., 8.

Duclaux[1] made experiments with mixtures of different volatile fatty acids, and came to the conclusion that each lower fatty acid of the series $C_n H_{2n+1} COOH$ had its own rate of distillation from a dilute aqueous solution.

Richmond[2] has criticised Duclaux's method of working and calculating the results, and has drawn up a formula by the aid of which the calculated values agree well with experimental results. He lays down the following laws :—(1) Each acid of this series behaves as a perfect gas on distillation from a dilute aqueous solution. (2) Each acid has a fixed rate of distillation which is an inverse function of its solubility in water, and is quite independent of the properties of the pure acids. (3) The apparent rate of distillation may be modified by condensation in the retort.

In order to obtain concordant results it is essential that the distillation should be carried out under specific conditions.[3] When only two acids are present the amount of each may be found from the results of the distillation, and the ratio between them calculated for each fraction. In the absence of other acids there should be a fairly close agreement between the ratios, and the mean ratio will give an indication of the molecular proportion.[4]

In one modification of the method, used by *Dyer*,[5] the volume of the aqueous solution is kept at a constant volume of 150 c.c. Under such conditions the results, when plotted on a logarithmic chart, form a straight line in the case of a single acid, but a curve when a mixture of acids is present, and the probable composition and approximate proportion of these acids may be found by reference to a chart.

Duclaux's method has also been criticised on the ground that practically identical results may be calculated by its means for mixtures of totally different proportions of acids, but it has been shown by *Lamb*[6] that figures based on the results obtained with pure acids are trustworthy, although not more than three acids can be satisfactorily estimated in the same fraction.

When a mixture of acids volatile with steam and others not volatile therewith is present, if, instead of blowing steam through the whole mass, the insoluble fatty acids are allowed to rise in a fused condition, and are then removed (after cooling and solidifying), the remaining aqueous liquor is often found to yield perceptibly less volatile acid, a portion having been dissolved by the insoluble acids, much as ether dissolves out various substances from aqueous solution when agitated therewith. In consequence of this, it is often impossible to obtain a constant weight of the insoluble fatty acids thus obtained on drying at 100° C., unless they have been repeatedly treated with boiling water, so as to remove soluble constituents (*vide* Chap. VIII., "Hehner Value"); otherwise, the small quantity of volatile acid present slowly evaporates, giving a continual small loss.

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[1] *Ann. Chim. Phys.*, (5); ii., 223.

[2] *Analyst*, 1895, xx., 193 and 217.

[3] *Ibid.*, 1908, xxiii., 305.

[4] *Ibid.*, 1917, xlii., 125.

[5] *J. Biol. Chem.*, 1917, xxviii., 445.

[6] *J. Amer. Chem. Soc.*, 1917, xxxix., 746.

In some cases this by and by becomes balanced by gain in weight through oxidation (by spontaneous absorption of oxygen from the air), and later on still the gain from this cause predominates.

INSOLUBLE FATTY ACIDS.

I. Separation of Liquid and Solid Acids.

Treatment of the Lead Salts with Ether.—Various methods of separation have been based upon the fact, first recorded by Varrentrapp, that the lead salts of the liquid fatty acids are much more soluble in ether than those of the solid fatty acids. These methods, however, only effect a fractional separation, although concordant results can be obtained by working under constant conditions. The iodine value (*q.v.*) is usually taken as an indication of the completeness of the separation effected.

Oudeman's Method.[1]—The fatty acids are dried on the water-bath with an excess of sodium carbonate, and the resulting mass completely extracted with successive portions of boiling alcohol. The filtered alcoholic solution of soap is diluted with water, and treated with an excess of lead acetate. The lead precipitate is dried and a weighed portion extracted with anhydrous ether in a closed flask, the extraction being repeated several times with fresh portions of ether. Finally the ethereal solution is evaporated, and the residue dried at a low temperature and weighed as lead oleate.

Kremel's Method.[2]—From 2 to 3 grammes of the fat are saponified with alcoholic potassium hydroxide, and the soap treated with a little water and exactly neutralised with acetic acid. After evaporation of the alcohol, the mass is dissolved in 80 c.c. of hot water, and a solution of lead acetate added.

The lead soap adheres to the sides of the flask on shaking, and, when cold, the supernatant liquid is filtered off and the deposit washed with hot water. The flask is next heated on the water-bath and the water poured off from the fused mass, after which ether is introduced in successive portions, and the ethereal solutions decanted through the filter, which is kept covered to prevent oxidation. The residue left on evaporation of the ether is dried first at a low temperature and then over sulphuric acid and weighed, and the amount of lead determined as lead oxide in an aliquot portion. The difference gives the weight of the anhydrides of the fatty acids present.

Röse's Method.[3]—With the object of simplifying these methods and preventing oxidation, Röse devised the following process:—1 gramme of the fatty acids is shaken with 0·5 gramme of litharge and 88 c.c. of ether in a stoppered flask, which is allowed to stand for 24 hours, with occasional agitation. The contents of the flask are then diluted to a definite volume, 50 c.c. of the liquid filtered into a weighed flask and evaporated, and the residue dried at a low temperature and weighed. The lead oxide it contains is then determined by warming it on the water-bath with 10 c.c. of dilute sulphuric acid (1 : 1), diluting the liquid with 80 c.c. of 95 per cent. alcohol, filtering, and drying the residue at 100° C. The molecular equivalent of the liquid fatty acids can be calculated from the amount of lead.

Twitchell[4] substituted petroleum spirit for ether in Röse's process, which effected a more perfect separation; but, in his opinion, the method is only reliable when the fat is quite fresh, and great care taken to prevent oxidation (*vide infra*).

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[1] *J. prakt. Chem.*, xcix., 407.

[2] *Pharm. Centralhalle*, v., 337.

[3] *J. Soc. Chem. Ind.*, 1887, vi., 306.

[4] *J. Amer. Chem. Soc.*, 1895, xvii., 289.

Muter and De Koningh's Method.[1]—Three grammes of the fat are saponified and the soap solution exactly neutralised with acetic acid, and run, with continual stirring, into a boiling mixture of 30 c.c. of lead acetate solution (1 : 10) and 200 c.c. of water. The lead soap is washed with hot water and shaken in a stoppered flask with ether (about 120 c.c. in all). After standing for twelve hours, with occasional shaking, the ether is filtered off into a Muter's tube (Fig. 32), and the precipitate washed with ether. The fatty acids in the ethereal extract are now liberated by shaking with water and hydrochloric acid, and the ethereal layer washed with water. The ethereal layer in the tube is then made up to 200 c.c. with ether, and 50 c.c. run off into an Erlenmeyer flask, partially evaporated, diluted with 50 c.c. of alcohol, and titrated with $\frac{N}{10}$ alkali, of which 1 c.c. corresponds to 0·0282 gramme of oleic acid.

For the determination of the iodine value, an aliquot portion of the ethereal extract is evaporated in a current of carbon dioxide, and the residue weighed and treated as in Hübl's method.

It was shown by *Hehner*[2] in a series of determinations with cotton-seed oil, coconut oil, etc., that no exact separation could be effected by methods based on the treatment of the lead salts with ether, since the solid fatty acids invariably showed a considerable iodine absorption. A similar conclusion had previously been arrived at by *Lewkowitsch*.[3]

Jean's Method.[4]—*Twitchell* (*loc. cit.*) recommends the following modification of Jean's method :—4 grammes of the fatty acids are dissolved in 50 c.c. of hot 95 per cent. alcohol, and 2·5 grammes of lead acetate dissolved in 20 c.c. of the same hot alcohol added. The resulting precipitate is allowed to stand for an hour, and then cooled to 15° C. for another hour. A portion of the filtrate is then treated with ether and hydrochloric acid, and the separated fatty acids washed and dried in a current of carbon dioxide, and the iodine value determined. The precipitate is washed with alcohol, decomposed with hydrochloric acid, and the iodine value of the solid fatty acids determined.

Twitchell obtained the comparative results in the examination of lard by different processes (see table).

Twitchell's experiments with Jean's process, making the filtration at a lower temperature, support his conclusion that there is a fractional precipitation, in which, first, the solid fatty acid, then the oleic, and, lastly, the linolic acids are precipitated.

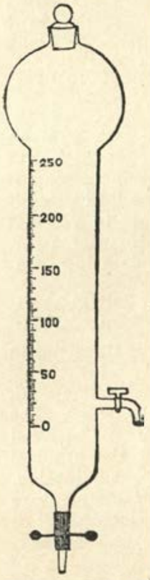

Fig. 32.
Muter's Tube.

In order to calculate the exact proportion of liquid acids from such results, he gives the following rules :—(*a*) The percentage of liquid acids in the alcoholic filtrate is calculated from the fraction drawn off. (*b*) This is multiplied by the iodine value of these acids, divided by 100, and subtracted from the iodine value of the original acids, the result representing oleic acid. (*c*) This result, divided by 0·9, gives the percentage of oleic acid precipitated with the solid acids, which is added to the liquid acids in the filtrate. Thus, in the example given above, 46·81 ÷ 100 × 109·35 = 51·19. Deducting this from 62·57 gives 11·38, which, divided by 0·9 = 12·64 per cent. of oleic acid in the precipitate. This, added to 46 81, gives 59·45 per cent. of total liquid fatty acids, the iodine value of which is $\frac{62\cdot57}{59\cdot45} = 105\cdot2$.

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[1] *Analyst*, 1889, xiv., 61.

[2] *Analyst*, 1892, xvii., 181.

[3] *J. Soc. Chem. Ind.*, 1890, ix., 845.

[4] *Chimie analytique des Matières Grasses.*

PROCESS.	Lard Fatty Acids.		Solid Fatty Acids.		Liquid Fatty Acids.	
	No.	Iodine Value.	Per cent.	Iodine Value.	Per cent.	Iodine Value.
Muter's, . .	i.	58·49-59·26	...	...	...	94·06
Jean's, . . .	i.	,,	46·24	4·9	51·81	103·37
,, (filtrated at 15° C.), .	ii.	62·57	53·19	...	46·81	109·35
,, (filtrated at 0° C.), .	ii.	,,	...	...	...	118·02
Röse's, . . .	ii.	,,	44·7	3·02	55·10	108·66
,, . . .	ii. (After 7 days)	,,	...	10·1	...	101·7

The linolic acid may be calculated from the iodine absorption of the liquid acids. 109·35 represents 78·5 per cent. of oleic acid and 21·5 per cent. of linolic acid. $\frac{21 \cdot 5 \times 46 \cdot 81}{100} = 10 \cdot 06$ per cent. of linolic acid.

The difference between the iodine values of the liquid fatty acids separated by Jean's and by Muter's process, as shown in the above table, is evidence that in the latter process considerable oxidation must have occurred. The effect of oxidation on Röse's process is shown in the last results, which were obtained with the fatty acids after being kept for seven days.

Treatment of the Lead Salts with Benzene.—*Farnsteiner*[1] has based a method of separation on the fact that the lead salts of unsaturated fatty acids are decidedly less soluble in benzene than in ether:—From 0·6 to 1 gramme of the fat is saponified with alcoholic potassium hydroxide, the alcohol expelled by evaporation, and the soap dissolved in 100 c.c. of boiling water and precipitated with 30 c.c. of a boiling solution of lead acetate containing about 1 gramme. The liquid is filtered when cold, the precipitate washed with cold water, which is subsequently removed as completely as possible. The residue is now dissolved in 50 c.c. of hot benzene, and the solution first allowed to stand for fifteen minutes, and then cool for two hours at 8° to 12° C.

The liquid is filtered through a tube covered with cotton-wool at the end (*cf. Determination of Stearic Acid*), and the flask washed out with 10 c.c. of benzene at 10° C., which is similarly expelled. The precipitate is then twice recrystallised in the same way from 25 c.c. of hot benzene, so that in all from 120 to 130 c.c. of the benzene filtrate are obtained.

The liquid fatty acids are liberated by the addition of 10 c.c. of dilute hydrochloric acid, the solution filtered through cotton wool, and the benzene evaporated in a current of hydrogen to prevent oxidation.

The solid fatty acids are determined by heating the insoluble lead

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[1] *Zeit. Untersuch. Nahr. Genussm.*, 1898, i., 390.

salts under a reflux condenser with 25 to 30 c.c. of benzene and dilute hydrochloric acid (1 : 10), then washing the solution of fatty acids and evaporating the benzene in a weighed flask.

The free fatty acids are dissolved in benzene, and the solution heated under a reflux condenser with powdered lead hydroxide prepared by precipitating a solution of lead acetate with sodium hydroxide, washing the precipitate with water, alcohol, and ether, and drying it at a low temperature. One part by weight of the solid fatty acids requires 0·4 part of lead hydroxide, and 1 part of liquid fatty acids 0·2 part.

Farnsteiner illustrates the accuracy of his method by the results (among others) given in the following table :—

Weight of Mixture taken.	Number of Precipitations.	Liquid Acids		Solid Acids		Remarks.
		Taken.	Found.	Taken.	Found.	
Gramme.		Per cent.	Per cent.	Per cent.	Per cent.	
0·7260	4	19·1	17·45	80·9	82·4	Old oleic acid.
0·6456	3	47·1	45·05	52·9	54·7	Liquid acids from olive oil.
0·6333	3	59·5	...	40·5	39·4	Liquid acids from cotton-seed oil.
0·7834	2	91·0	89·4	9·0	10·8	Nearly pure oleic acid.

Farnsteiner also refers to Twitchell's method of calculating the amount of liquid fatty acids (*vide supra*), and gives the following formula for arriving at the result from the two iodine values—

$$x = \frac{100\ \mathrm{J}}{\mathrm{J}_1};$$

where J represents the iodine value of the original substance, and J_1 that of the liquid fatty acids.

Determination of the Iodine Value of the Liquid Fatty Acids.—The risk of oxidation is greatly minimised by determining the iodine value of the liquid acids while still in solution in the benzene. *Farnsteiner* [1] has found that benzene, from which all thiophene has been removed, absorbs no iodine, and on this fact bases the following method :—From 1 to 2 grammes of the lead salts are dissolved in 100 c.c. of warm benzene (free from thiophene [2]). As soon as a precipitate begins to form the flask is left for two hours at 8° to 12° C., and the liquid filtered. The filtrate is treated with dilute hydrochloric acid and water, and the benzene solution of the liberated fatty acid washed twice with water, and filtered. Of this filtrate two portions of 25 c.c. are treated with Hübl's solution in the usual way, whilst a similar third portion is evaporated in a current of hydrogen, and the residue weighed, in order to determine the quantity of fatty acids in the other fractions.

Treatment of the Zinc Salts with Carbon Bisulphide (*Sear's Method*).—10 grammes of the fatty acids are dissolved in 200 c.c. of carbon bisulphide, and

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[1] *Zeit. Untersuch. Nahr. Genussm.*, 1898, i., 529.

[2] Heusler (*Zeit. angew. Chem.*, 1896, 750) frees benzene from thiophene by heating 120 c.c. to the boiling point with 5·8 grammes of aluminium chloride, and then distilling, care being taken to exclude moisture. The distillate is washed with sodium hydroxide solution, and dried with calcium chloride.

the solution shaken at intervals for six hours, and filtered. The filter is washed with carbon bisulphide, the filtrate and washings evaporated in a weighed flask, and the residue dried at 90° C. The combined zinc is determined by decomposing the salts with 50 c.c. of N-sulphuric acid, diluting the acid layer to 200 c.c., and titrating an aliquot portion with N-sodium hydroxide solution. From the result the weight of zinc combined with 100 grammes of the fatty acid can be calculated, and also the molecular equivalent in terms of zinc oxide.

The following results, selected from a number obtained by *Halphen*,[1] show the degree of separation thus effected :—

FAT.	Iodine Value of Mixed Fatty Acids.	Iodine Value of "Liquid" Fatty Acids.	Iodine Value of "Solid" Fatty Acids.	"Liquid" Fatty Acids per cent.	"Solid" Acids per cent.	Saponification Equivalent in ZnO per cent.
Lard, . .	63·5	91·95	28·83	57·14	42·86	14·7
Mutton suet, .	37·84	80·26	17·52	31·44	68·56	14·5
Cotton-seed oil, .	102·36	129·03	49·53	69·06	30·99	14·9

It is obvious that no quantitative separation is possible by this method, and the same remark applies to the following method :—

Treatment of the Zinc Salts with Ether (*Jean's Method*).—The fat is saponified, the excess of alkali neutralised with acetic acid, and the alcohol evaporated on the water-bath. The soap is dissolved in hot water, and precipitated by means of a hot solution of zinc acetate (1 part to 2 parts of fat). The zinc soap is washed with hot water and alcohol, pressed between filter-paper, and extracted with about ten times its volume of anhydrous ether for fifteen to thirty minutes under a reflux condenser. The ethereal extract is decomposed with dilute hydrochloric acid, and the solution containing the liberated fatty acids washed with water and evaporated in a weighed flask, with every precaution to prevent oxidation. The residue is weighed, and its iodine value determined in the usual way.

Iodine Value of the Zinc Salts.—*Bömer*[2] has shown that the iodine value of the zinc salts may be determined directly without previous liberation of the fatty acids. He points out that since the molecular equivalents of the higher unsaturated fatty acids differ but slightly, the molecular equivalent of the mixed zinc salts may be taken as that of zinc oleate (627·1) without risk of considerable error; and since 100 parts of zinc oleate correspond to 89·94 parts of oleic acid, the iodine value of the liquid fatty acids (regarded as oleic acid) may be calculated by dividing the value of the zinc salts by 0·8994, or multiplying it by 1·112. The advantage of this method is that the risk of oxidation of the liquid fatty acids is reduced to a minimum.

Treatment of the Mixed Fatty Acids with Sulphuric Acid.—*Twitchell*[3] based a method of separation on the fact that the sulphonated compounds formed on treating unsaturated fatty acids are insoluble in petroleum spirit, whereas the saturated acids can be readily extracted. He treats 1 gramme of the melted fatty acids with 3 c.c. of 85 per cent. sulphuric acid, in a flask chilled in ice-water, and allows the temperature to rise gradually. As soon as a clear solution is obtained the flask is again cooled, and its contents extracted with petroleum spirit, which, on evaporation, is stated to leave a residue of the saturated fatty acids.

Lewkowitsch[4] subjected this method to a critical examination, and showed that it was far from yielding quantitative results.

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[1] *J. Pharm. Chim.*, 1894, xx., 241.

[2] *Zeit. Untersuch. Nahr. Genussm.*, 1898, i., 541.

[3] *J. Soc. Chem. Ind.*, 1897, xvi., 1002.

[4] *Analyst*, 1900, xxv., 64.

Separation as Ammonium Salts.—*David*[1] has based a method of separating solid from liquid fatty acids on the fact that ammonium salts of the former are completely insoluble in a large excess of ammonia solution at 13° to 14° C. About 2 grammes of the fatty acids are dissolved in 5 c.c. of 95 per cent. alcohol, the solution treated with 50 c.c. of ammonia solution, and the liquid heated until bubbles of gas appear, after which it is allowed to stand for several hours at 14° C., and then filtered from the insoluble ammonium palmitate and stearate. The precipitate is washed with ammonia solution, then with dilute hydrochloric acid (1 : 1), and, finally, with water, dried at 100° C., and weighed. In test experiments with mixtures containing 60 per cent. of solid fatty acids the amounts recovered were 59·7 to 59·8 per cent. Hydroxystearic acid, iso-oleic acid, lauric acid, and arachidic acid also yield insoluble ammonium salts.

In *Falciola's*[2] method alcohol is used as the solvent for separating the ammonium salts. The mixed fatty acids are dissolved in ether, and the solution treated with ammonia gas, and cooled to about 15·5° C. The solvent is evaporated, and the residue mixed with about four times its volume of ammoniacal alcohol at about 0° C., and filtered with the aid of a pump. The residue is washed with chilled absolute alcohol, the filtrate and washings treated with dilute hydrochloric acid, the solvent evaporated, and the liquid fatty acids washed, dried, and weighed. The solid fatty acids on the filter are also separated and weighed. The accuracy of which the method is capable is shown by the following example :—A mixture of 5 grammes of oleic acid, 2·5 grammes of stearic acid, and 2·5 grammes of palmitic acid was treated as described, and the separated oleate was found to contain 0·2 gramme of ammonium palmitate and 0·04 gramme of ammonium stearate.

The method does not give good results with the fatty acids of certain oils, as, for example, olive oil, which leaves no insoluble ammonium salts on the filter.

Fachini and Dorta's Method.—A method of effecting an approximate separation of solid from liquid acids has been based by *Fachini* and *Dorta*[3] on the relative insolubility of the potassium soaps of the former in actone. Ten grammes of the fatty acids are disssolved in 90 c.c. of boiling acetone, and the clear solution treated at boiling point with 10 c.c. of aqueous N-potassium hydroxide solution and allowed to cool at 15° C. The crystals are separated, with the aid of a pump, and washed with small amounts of pure acetone, and the fatty acids liberated. By adding insufficient potassium hydroxide to combine with all the fatty acids present arachidic acid may be separated from the fatty acids of arachis oil in a single precipitation.

It has been shown by *de Waele*[4] that this method effects a more

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[1] *Comptes rend.*, 1910, cli., 756.

[2] *Gazz. Chim. Ital.*, 1910, xl., 217, 425.

[3] *Chem. Zeit.*, 1914, xxxviii., 18.

[4] *Analyst*, 1914, xxxix., 389.

complete separation of the solid and liquid fatty acids than the lead-ether method. Both methods fail in the case of polymerised oils, the liquid fatty acids of which behave in the same way as solid fatty acids.

II. Separation of Palmitic and Stearic Acid from Oleic Acid.

Calculation of Oleic Acid from the Iodine Value.—When a mixture of fatty acids is known to contain no other unsaturated fatty acid than oleic acid, it is possible to calculate the percentage of the latter from the iodine value as was first shown by Hübl. The theoretical iodine absorption of pure olein is 86·20 and of pure oleic acid 90·07, and hence the percentage of oleic acid can be calculated by means of the formulæ—

$$O = \frac{100}{86{\cdot}20} \cdot J = 1{\cdot}1601\ J$$

and

$$A = \frac{100}{90{\cdot}07} \cdot J_1 = 1{\cdot}1102\ J_1,$$

where O represents the percentage of olein, A the percentage of oleic acid, J the iodine value of the fat, and J_1 the iodine value of the free fatty acids.

Unfortunately we have no means of proving with certainty that a mixture contains only oleic acid; on the other hand, there is good ground for concluding that linolic acid (with an iodine value of 181·43) is a much more frequent constituent of fats and oils than it was formerly supposed to be.

Treatment of the Fatty Acids with a Mixture of Alcohol and Acetic Acid (*David's Method*).—*David*[1] based a method of separation on the fact that stearic and palmitic acids are much less soluble than oleic acid in a mixture of alcohol and acetic acid. To obtain the right strength 1 c.c. of pure oleic acid and 3 c.c. of 95 per cent. alcohol are placed in a graduated cylinder and a mixture of equal volumes of acetic acid and water added, drop by drop, so long as no turbidity is produced. The alcohol and dilute acetic acid are now mixed in this ascertained proportion (say 300 : 200), 1 to 2 grammes of pure stearic acid introduced, and the clear liquid poured off from the undissolved portion.

In making a determination a weighed quantity of the finely-divided fat is shaken in a stoppered flask at 15° C. with the solvent thus prepared, and then allowed to stand for twenty-four hours at 15° C. The liquid is then filtered, and the insoluble residue washed on the filter, first with the prepared solvent, and then with cold water, and heated on the water-bath in a basin. The cake which is formed on the surface of the water is finally separated, dried at 100° C., and weighed.

In this way tallow and palm oil were found to contain about 95 per cent. of solid fatty acids.

Hehner and *Mitchell*[2] have made experiments with this method,

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[1] *Comptes Rendus*, lxxxvi., 1416.

[2] Unpublished.

and have found that the results cannot be relied upon, mainly because the inevitable variations of temperature cause a greater or less amount of the solid fatty acids to pass into solution.

Fractional Distillation.—By means of superheated steam the fatty acids of higher molecular weight may be fairly readily distilled; but anything like a complete separation of closely related homologous acids (*e.g.*, myristic, palmitic, and stearic acids) in this way by processes of fractional distillation is difficult, if not impossible; and the same remark applies to distillation under greatly diminished pressure (in a partial vacuum).

Hehner and the writer have made a number of experiments [1] on the distillation of different fatty acids in a current of superheated alcohol. The following table gives some of their results [1]:—

Fatty Acid.	Began to Distil at °C.
Commercial oleic acid, ...	168
,, stearic acid, ...	165
Pure stearic acid, ...	160-165
,, palmitic acid, ...	125
Butter fatty acids, ...	105-125
Oleomargarine fatty acids, ...	125-160

Attempts to effect any sharp separation of the different fatty acids in this way were unsuccessful.

This is also shown by the results obtained by *Bull*,[2] who effected a partial separation of the fatty acids of marine animal oils by heating them to about 200° C., and then introducing a current of superheated steam, first at 200° C., and afterwards at successively lower temperatures down to 100° C.

It was found that the brown oxidised fatty acids were not volatile with superheated steam, and as the free acids are readily oxidised Bull preferred a method of fractional precipitation of the sodium and potassium salts (*vide infra*).

The following results obtained with the potassium salts of cod-liver oil insoluble in alcohol illustrate this method of fractional distillation:—

Temperature.	Weight.	Acid Value.	Iodine Value.
°C.	Grammes.		
160	83·3	182·0	102 6
149	95·5	200·0	62·4
120	115·7	209·0	40·0
100	14·2	212·0	33·0

Saturated fatty acids were present in all the fractions, stearic acid predominating the first, and palmitic acid and its lower homologues in the third and fourth.

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[1] Unpublished.

[2] *Chem. Zeit.*, 1899, xxiii., 996.

Fractional Saturation with Alkali.—In some cases fractional saturation with alkali, etc., of a mixture of acids will cause a more or less complete separation, one acid combining with the base to the exclusion of the other; more often the base becomes shared between the two in proportions depending on the relative masses present. Thus *Thum* found[1] that when a mixture of equal weights of stearic and oleic acids was dissolved in hot alcohol and treated with a quantity of alcoholic potassium hydroxide sufficient to saturate only one-half of the total acids, a mixed soap was obtained, which (when separated from the uncombined excess of fatty acids by means of petroleum ether) consisted substantially of equal quantities of potassium stearate and oleate; the free acids similarly consisting of stearic and oleic acids in practically the same proportion.[2]

Fractional Precipitation (*Heintz*).—With a mixture of solid fatty acids (palmitic, stearic, arachidic, etc.), fractional crystallisation from alcohol of the mixed free acids; fractional precipitation as insoluble salts (of lead, magnesium, etc.); fractional crystallisation of certain salts (*e.g.*, magnesium salts) from alcohol or other appropriate solvent; and similar processes are applicable in various cases; but the complete examination of mixtures of fatty acids in this way is so laborious, that it has been thoroughly carried out in but very few instances. In the case of fractional precipitation, as a general rule, the acid of higher molecular weight precipitates first; thus, with a mixture of arachic, stearic, and palmitic acids in approximately equal proportions, precipitated as salts in several fractions, the first fraction will be chiefly a salt of arachic acid, and the last will contain little besides palmitate.

Hehner and *Mitchell*[3] made experiments to determine to what extent Heintz's method was capable of effecting a concentration of the fatty acid of higher molecular weight from a mixture of known composition by one precipitation.

Mixtures of pure stearic and palmitic acids were dissolved in hot (methylated) alcohol, and a sufficient amount of an aqueous solution of barium acetate exactly to precipitate the stearic acid, added drop by drop, with continual agitation. After cooling, the precipitates were filtered off, washed with cold 98 per cent. alcohol, dried in the water-oven, and the barium present determined by ignition with sulphuric acid. From the weight of barium sulphate obtained the molecular equivalent of the fatty acids was calculated, and from this the amount of stearic acid by the formula—

$$x = \frac{284\,(m - 256)}{m\,(284 - 256)};$$

where x represents the required amount of stearic acid, m the molecular equivalent found, and 284 and 256 the respective equivalents of stearic and palmitic acids.

The filtrate and washings from the first precipitate were mixed, and a second fraction precipitated and treated as before. In some cases a third and fourth

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[1] *Zeit. angew. Chem.*, 1890, 482.

[2] A similar result is obtained when a given fatty acid acts on a mixture of potassium hydroxide and sodium hydroxide; both potassium and sodium soaps result in proportions approximating those in which the two alkalis are present in the mixture; and not one kind of soap to the exclusion of the other (*vide* Chap. XXI.).

[3] *Analyst*, 1896, xxi., 317.

precipitation was made. Some of the results thus obtained are given in the following table:—

Taken.		Barium Acetate Solution 8·94 Grammes in 100 cc.	Molecular Equivalent of acids in Precipitate.	Per cent. of Stearic Acid in Precipitate.	Weight of Recovered Stearic acid.
Stearic Acid.	Palmitic Acid.				
Grammes.	Grammes.				Grammes.
1	1	5 c.c.	275·5	71·7	0·549
		5 c.c.	261·75	22·2	0·076
					0·625
1	2	5 c.c.	272·9	62·8	0·5039
		5 c.c.	273·0	63·0	0·4983
		5 c.c.	261·6	22·3	0·0904
					1·0926
1	3	5 c.c.	263·2	27·9	0·1953
		5 c.c.	267·3	42·8	0·3097
					0·5050

These results were also confirmed by taking the melting points of the mixed fatty acids obtained from the precipitate. Similar experiments with magnesium acetate as the precipitant also showed that, although by oft-repeated fractionation of a mixture of fatty acids, it could be separated into its pure constituents, yet no sharp separation could even be approximately obtained, however slowly the precipitation was made to take place. When more than two fatty acids were present, the results would be still more uncertain.

This is also shown by the following results, obtained by *Bull*[1] on treating the sodium and potassium salts of white cod-liver oil with different solvents:—

Fatty Acids.	Weight.	Acid Value.	Iodine Value.
	Grammes.		
A. In the potassium salts insoluble in alcohol, .	334	194·2	67·5
B. In sodium salts insoluble in alcohol, . .	375	190·0	135·6
C. ,, ,, soluble in ether, . . .	120·0	167·0	322·4
D. ,, ,, insoluble in ether, . .	69·0	169·0	347·0

The fatty acids, A, contained nearly the whole of the saturated fatty acids, together with acids of the oleic series: B consisted of acids of the oleic and linolic series, and C essentially of acids of the series $C_n H_{2n-8}O_2$ and $C_n H_{2n-10}O_2$.

Treatment of the Fatty Acids with Dilute Alcohol.—*Hehner* and *Mitchell*[2] effected an approximate separation of stearic acid from other fatty acids by triturating 10 grammes of the fatty acids in a mortar with 100 c.c. of dilute alcohol (sp. gr., 0·911) at 15° C., when it was found that the unsaturated fatty acids were completely dissolved, the palmitic acid partially so, whilst the stearic acid remained almost completely undissolved. The residue was washed with alcohol of the same

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[1] *Chem. Zeit.*, 1899, xxiii., 996.

[2] *Analyst*, 1896, xxi., 320.

strength, dried between filter-paper, and subsequently in the water-oven, and its molecular equivalent determined by titration with alcoholic alkali. From the results, the proportion of stearic acid was calculated by means of the formula given above :—

$$x = \frac{284\,(m - 256)}{m\,(284 - 256)}.$$

The objections to this method are that variations in the temperature during the treatment of the mixed acids lead to a larger residue being left behind, whilst the calculation of the percentage of stearic acid from the molecular equivalent (Hausmann's method) has the drawback that a very slight error in the titration (0·1 c.c.) causes an error of more than 3 per cent. in the final result.

Calculation of Proportion of Fatty Acids from Iodine Value and Molecular Weight.—*Mayer* [1] gives the following formula for calculating the composition of a mixture containing only oleic, palmitic, and stearic acids, from the iodine value and the molecular equivalent :—

$$x + y = 100 \quad \mathrm{O},$$

$$\frac{x}{284} + \frac{y}{256} + \frac{\mathrm{O}}{282} = \frac{100}{m},$$

$$x = \frac{m(1{,}001{,}100 - 923\,\mathrm{O}) - 2{,}562{,}806}{987m},$$

in which O represents the amount of oleic acid calculated from the iodine value, and x and y the respective percentages of stearic and palmitic acids.

Calculation of Composition of a Mixture of Two Fatty Acids from their Mean Neutralisation Number.—In certain cases where the substance examined is known to be a mixture of two different fatty acids, the relative amounts of the two constituents can be at least approximately calculated from their mean neutralisation value. Thus, in the case of a mixture of *palmitic acid* (molecular weight = 256) and *stearic acid* (284), let the neutralisation number of the mixture be n; the mean molecular equivalent of the mixture will accordingly be $\frac{56{,}100}{n}$. Hence the following table gives the relative proportions of the two acids :—

Mean Molecular Equivalent.	Percentage of	
	Palmitic Acid.	Stearic Acid.
256	100	0
258·8	90	10
261·6	80	20
264·4	70	30
267·2	60	40
270·0	50	50
272·8	40	60
275·6	30	70
278·4	20	80
281·2	10	90
284·0	0	100

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[1] *Chem. Zeit.*, viii., 1667.

The following formula gives the same result:—Let S be the percentage of stearic acid, and M the mean molecular weight; then

$$S = 100\frac{284\,(M - 256)}{M\,(284 - 256)}.$$

In similar fashion the relative proportions of any other two fatty acids in a mixture containing only those two can be calculated.

This method is open to the objections mentioned above.

Direct Determination of Stearic Acid.—The method described below was based by *Hehner* and *Mitchell*[1] on the fact that alcohol saturated with pure stearic acid at a definite temperature is unable to dissolve any more of that compound, although it can still take up a considerable quantity of other fatty acids. Stearic acid is soluble in alcohol of specific gravity 0·8185 to the extent of 0·155 gramme in 100 c.c. at 0° C., whilst the solubility of palmitic acid is about 1·298 grammes, or approximately eight times as great.

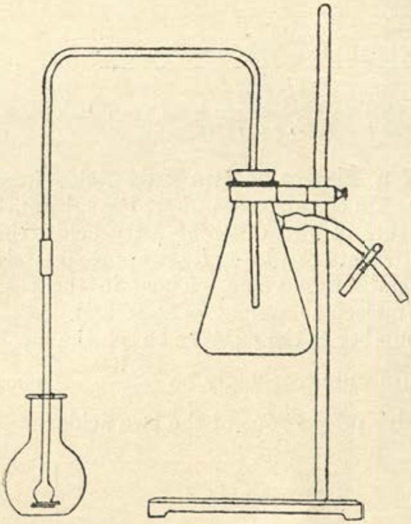

Fig. 33.—Apparatus for Stearic Acid Determination.

For the preparation of the stock solution about 3 grammes of pure stearic acid were dissolved in warm (methylated) alcohol of specific gravity 0·8183 (= 94·4 per cent. by volume), and the stoppered bottle immersed in a mixture of ice and water contained in a metal box protected by means of flannel and sawdust, and fitted into a wooden chest. After twelve hours the saturated liquid was siphoned off without removing the bottle from the ice-water, by means of an apparatus on the principle of that shown in Fig. 33. In the actual determinations the thistle-funnel was about $\frac{1}{4}$ inch in diameter, and was covered with linen to serve as a filter.

The fatty acids (0·5 to 1 grm.) were mixed with 50 to 100 c.c. of the saturated solution and the flask closed with a rubber cork, and these cautiously warmed until a clear solution was obtained. It was then clamped in the ice-water and left till next morning, when the alcohol was filtered off with the aid of suction by means of the apparatus shown in the figure. The residue was washed three times with 10 c.c. of saturated alcohol previously cooled to 0° C., and the washings removed each time as before. The small funnel was then

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[1] *Analyst*, 1896, xxi., 321.

detached from the suction apparatus, and washed with hot alcohol, the washings falling into the flask which contained the residue, the flask having been previously removed from the ice-chest. The alcohol was then evaporated and the residue dried at 100° C. until constant in weight. A correction, experimentally found to be 0·005 gramme, was deducted to allow for the stearic acid left from the saturated alcohol clinging to the sides of the flask and the funnel.

The accuracy of which this method is capable is shown in the following table of results selected from the numerous tables given in the original paper :—

Stearic Acid taken.	Fatty Acid.	Stearic Acid found after deducting 0·005 grm.
0·0556	Butyric acid, 5 c.c., . .	0·0582
0·106	Coconut oil acids, 0·9 grm., .	0·118
0·2026	Palmitic acid, 0·547 grm., .	0·2032
0·2997	Crude oleic acid, 3·2 grm., .	0·3027

The following amounts of stearic acid were obtained in the examination of various commercial fats and oils by this method :—Commercial stearic acid, 47 to 50·6 per cent. ; lards, 6 to 13 per cent. ; beef stearine, 51 per cent. ; oleomargarine, 22 per cent. ; margarine (2), 11·7 and 24·8 per cent. ; horse-fat, no deposit ; cotton "stearine," 3·3 per cent. ; stillingia tallow, no deposit ; coco-butter, 40 per cent. ; maize, almond, and olive oils, no deposits ; and earth-nut oil, 7 per cent. In the case of butter no deposit was, as a rule, obtained ; but in some instances there was a considerable one (*cf. Butter*).

The fatty acid obtained from Japan wax, which, from its melting point and molecular equivalent, appeared to be palmitic acid, had a very remarkable influence on the crystallisation. It not only yielded no deposit itself, but prevented the deposition of stearic acid, even when the latter was present to the extent of 0·15 gramme.

Emerson[1] finds that the chief difficulty in this method is to obtain a saturated solution of stearic acid in alcohol. In order to obtain accurate results by the method, in the case of small amounts of stearic acid, he adds a known quantity of the pure acid sufficient to bring the total quantity up to at least 6·7 grammes per 100 c.c. or 0·5 gramme per 50 c.c. of solvent. This has been confirmed by *Holland*, *Reed*, and *Buckley*,[2] who have found that the addition of a known quantity of pure stearic acid obviates the effect of supersaturation of the solution. They have found that lauric, myristic, and oleic acid do not affect the results, but that palmitic acid increases the solubility of the stearic acid, and has an influence on the crystalline structure of the precipitate. This may be obviated to a large extent by increasing the relative proportion of stearic acid.

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[1] *J. Amer. Chem. Soc.*, 1907, xxix., 1750.

[2] *J. Agric. Research*, 1916, vi., 101.

III. Separation and Estimation of Liquid Fatty Acids.

Determination of Oleic Acid.—Barium oleate is not very soluble in a mixture of cold benzene and alcohol, and on this fact *Farnsteiner*[1] has based a method of estimating the acid. The fat is saponified, and barium chloride added to the hot soap solution. The washed precipitate is dissolved in 50 c.c. of hot benzene containing 2·5 c.c. of 95 per cent. alcohol. The precipitate which forms on cooling is re-crystallised from 50 c.c. of benzene containing 10 c.c. of alcohol, and the resulting precipitate again re-crystallised from a mixture of 50 c.c. of benzene and 20 c.c. of alcohol. The fatty acids separated from the insoluble salts consist of oleic and saturated fatty acids which can be separated by Farnsteiner's method of treating the lead salts with benzene (*vide supra*). The barium salts can also be obtained by saponifying the fat with a solution of barium hydroxide in equal volumes of benzene and methyl alcohol.

Lewkowitsch[2] has shown that, owing to the fact that barium oleate is not completely insoluble in benzene, this method does not yield reliable results.

Mitchell[3] has suggested the use of a solvent previously saturated with pure barium oleate at a definite temperature, the determination to be made in the same way as in the case of stearic acid (*supra*).

Determination of Linolic Acid.—If an unsaturated substance is known to contain only oleic and linolic acids the proportion of the latter may be calculated from the iodine or bromine absorption by means of the formula

$$\frac{181{\cdot}43\,x}{100} + \frac{(100 - x)\,90{\cdot}07}{100} = m;$$

where x represents the required percentage of linolic acid, m the observed iodine value, and 181·43 and 90·07 the respective iodine absorptions of linolic and oleic acids.

Gravimetric Determination.—According to *Farnsteiner*[4] linolic tetrabromide is only soluble in petroleum spirit to the extent of 0·014 gramme in 100 c.c. at 12·5° C., or 0·008 gramme at about 0° C.; and on this he bases the following method:—A weighed quantity of the liquid fatty acids obtained by his method of separation (*vide supra*) is dissolved in chloroform or petroleum spirit and brominated. The solvent and excess of bromine are evaporated, and the residue dissolved in petroluem spirit, cooled down to 12° C., and the deposit re-crystallised from petroleum spirit, collected, dried, and weighed.

In this way, under varying conditions, cotton-seed oil yielded a bromide (m.p. 113° to 114° C.) corresponding to 17·3 to 18·9 per cent. of linolic acid. With other oils the following percentages were found:—Sesamé oil, 15·2 to 16·4; earth-nut oil, about 6; almond oil, 5·97; mustard-seed oil, about 4·5; horse-fat (liquid acids); olive oil, trace; lard, small quantity; and butter fat, none.

Determination of Linolenic Acid (*Direct Methods*).—*Hehner* and *Mitchell*[5] dissolved 0·2 to 0·3 gramme of the total fatty acids in 10 c.c. of acetic acid, and cooled the solution to 5° C. in a corked flask. Bromine was then added, drop by drop, until a permanent reddish colour was perceptible. After standing for three hours the liquid was filtered through a Soxhlet-tube containing asbestos, and the deposit

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[1] *Zeit. Untersuch. Nahr. Genussm.*, 1899, ii., 1.

[2] *Analyst*, 1900, xxv., 64.

[3] *Flesh Foods*, 100.

[4] *Zeit. Untersuch. Nahr. Genussm.*, 1899, ii., 1.

[5] *Analyst*, 1898, xxiii., 313.

washed with chilled acetic acid, alcohol, and ether (5 c.c. of each), and dried in the water oven until constant in weight.

The results obtained by this method (see *Linseed Oil*) are fairly satisfactory if the same conditions of working be observed, but when any larger quantity of the fatty acids are used linolic tetrabromide is apt to come down simultaneously; to wash this out of the linolenic hexabromide requires considerable quantities of solvent, in which the hexabromide is not completely insoluble.

A more reliable method is to obtain the mixture of solid compounds, to wash this but slightly to remove the readily soluble oleic dibromide, and then to determine the percentage of bromine in the dried and weighed precipitate. From the amount of bromine found the percentage of linolenic hexabromide in the mixture is calculated by means of the formula

$$\frac{63 \cdot 3\, x}{100} + \frac{(100 - x)\, 53 \cdot 3}{100} = m,$$

in which x represents the required percentage of hexabromide, m the percentage of bromine in the mixed deposit, and 63·3 and 53·3 the respective percentages of bromine in pure linolenic hexabromide and linolic tetrabromide.

By these methods linseed oil fatty acids yielded from 18 to 23 per cent. of hexabromide; rape-seed oil fatty acids, 3·6 per cent.; and cod-liver oil acids, 18 per cent. of similar compounds.

Farnsteiner,[1] in his experiments on the determination of linolic acid (*vide supra*), obtained from certain oils and fats bromides insoluble in petroleum spirit, which, from their melting points, he concluded to be linolenic hexabromide. Thus it was isolated in small quantity from rape-seed oil and olive oil. In the case of mustard-seed oil the amount corresponded to 4 per cent. of linolenic acid, whilst traces of the same compound were isolated from the liquid fatty acids of butter fat, lard, and tallow.

Determination of Highly Unsaturated Fatty Acids.—*Treatment of the Sodium Salts with Ether.*—*Bull*[2] describes the following method of determining the amount of highly unsaturated acids (mainly belonging to the groups $C_n H_{2n-8}O_2$ and $C_n H_{2n-10}O_2$) in marine animal oils:—

Seven grammes of the oil are boiled on the water-bath under a reflux condenser for thirty minutes with 25 c.c. of a solution of 23 grammes of pure sodium in a litre of absolute alcohol. After standing for two hours the soap is broken up and treated with 144·2 c.c. of anhydrous ether, the mixture being shaken in a closed flask at intervals during about thirty minutes.

The liquid is then filtered, an aliquot portion of the filtrate withdrawn, and the unsaponifiable matter separated by shaking the liquid with three successive portions of 20 c.c. of water in a separating-funnel, any dissociation of the sodium salts being prevented by adding

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[1] *Chem. Zeit.*, 1899, xxiii., 1043.

[2] *Chem. Zeit*, 1899, xxiii., 1043.

a trace of alkali. The fatty acids are then recovered from the aqueous extract in the usual manner, leaving the unsaponifiable matter in solution in the aqueous layer.

To prevent oxidation the fatty acids are dried at 60° to 70° C. in a weighed round-bottomed flask with the aid of a vacuum pump and constant shaking.

The following results, among others, were thus obtained :—

Oil.	Acid Value.	Saponification Value.	Iodine Value.	Specific Gravity at 15° C.	Unsaponifiable Matter.	Highly Unsaturated Fatty Acids.	Acid Value of.	Iodine Value of.
					Per cent.	Per cent.		
Cod-liver, Japan, .	5·68	184·7	140·8	0·9272	2·67	11·61	182·8	341·8
,, ,, White, Lofoden,	13·0	183·7	144·6	0·9232	2·16	17·22	202·2	314·0
,, ,, Crown, Hamburg,	31·9	175·2	147·9	0·9310	7·89	13·04	193·7	319·5
Sardine, Japan, . .	2·2	189·0	134·1	0·9283	1·96	12·12	188·2	285·8
Herring, ,, . .	1·8	170·9	131·0	0·9215	10·68	10·48	175·0	296·2
,, England, .	40·2	184·8	132·7	0·9391	2·64	11·49	194·0	317·0
Arctic whale, refined,	1·9	185·0	117·4	0·9234	2·11	7·19	206·3	300·3
,, ,, crude, .	2·5	183·9	127·4	0·9222	1·37	8·83	201·4	275·5
Porpoise body, . .	0·75	203·4	126·9	0·9266	2·01	14·3	313·2	285·4
Sunfish, . . .	2·15	147·6	102·7	0·9010	24·12	10·66	...	340·5
Sturgeon, . . .	0·23	186·3	125·3	0·9236	1·78	9·53	199·7	281·6
Shark, Japan, . .	0·88	163·5	136·0	0·9177	12·54	8·57	183·0	312·5
Seal, ...	0·77	190·6	143·4	0·9266	0·83	11·96	182·8	330·0

Specimens of refined linseed, olive, and rape oils only contained small proportions (1·32 to 2·37 per cent.) of acids forming ether-soluble salts, as was to be expected.

Characteristic Oxidation Products.—In certain cases the results furnished by cautious oxidation afford useful indications of the nature of the fatty acids ; this is more especially the case when an approximate separation of liquid and solid fatty acids has been previously effected by conversion into lead salts and treatment with ether, so as to dissolve out oleate and linolate of lead, etc., leaving undissolved lead stearate, palmitate, etc.

Hazura's[1] method is as follows :—The fatty acids (say 30 grammes) obtained by decomposing the lead salts that dissolve in ether, are saponified, and the soap dissolved in 2 litres of water and very gradually oxidised with 2 litres of a 1·5 per cent. solution of potassium permanganate with continuous agitation. After ten minutes a current of sulphur dioxide is passed in until the liquid becomes acid and all the precipitated manganese dioxide has dissolved.

The products of oxidation of oleic and linolic acids (dihydroxystearic and sativic acids) are only very sparingly soluble, and con-

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[1] *Monatsh. f. Chem.*, 1888, ix., 180, 469, 475, 944 ; 1889, x., 190.

sequently are precipitated; whilst linusic and isolinusic acids (the oxidation products of linolenic and isolinolenic acids respectively) remain in solution. These latter acids are extracted by neutralising with potassium hydroxide, evaporating to a small bulk (one-twelfth to one-fourteenth of the original volume) and decomposing with sulphuric acid. The precipitate is dried in the air, treated with ether to dissolve out readily soluble substances, and the residue crystallised from alcohol and from water so as to separate the more soluble isolinusic acid from the less soluble linusic acid.

Dihydroxystearic acid and sativic acid are separated in a similar way from the precipitate thrown down in the earlier stage. The precipitate is washed with a little ether to remove easily soluble fatty acids (unoxidised) and then treated with large amounts of ether (100 parts of ether to 1 of substance). Dihydroxystearic acid is chiefly dissolved out, and can be obtained by evaporation and re-crystallisation of the deposited crystals from alcohol twice in succession; whilst sativic acid is isolated from the insoluble portion by boiling with water, filtering while boiling hot, and crystallisation on cooling. The purified acids thus obtained are further identified by means of their melting points (p. 51). The acetylation test (Chap. VIII.) may also be usefully employed for this purpose.

In somewhat similar fashion trihydroxystearic and isotrihydroxystearic acids can be obtained from the fatty acids of castor oil. It is noteworthy in this connection that the acids obtained by the oxidation of isoleic acid and of elaidic acid (the isomeride of oleic acid produced by the action of nitrous acid) are dihydroxystearic acids, isomeric but not identical with that obtained from ordinary oleic acid (*Saytzeff*). Similarly, the oxidation products of erucic acid and its elaido derivative brassic acid, yield two isomeric dihydroxybenic acids (*q.v.*). *Hazura* also made use of the difference in solubility of the barium salts of the hydroxy acids to effect a separation, linusic and insolinusic acids being readily soluble in boiling water, whilst dihydroxystearic and sativic acids are insoluble.

Fahrion's Modification.—*Fahrion* recommends petroleum spirit for the separation of saturated and unoxidised unsaturated fatty acids from the hydroxy derivatives, his method being as follows:—10 grammes of the fat are saponified with 10 grammes of sodium hydroxide with the aid of alcohol. The soap solution is evaporated to dryness, and the residue dissolved in a litre of boiling water. This solution is oxidised with a 5 per cent. solution of potassium permanganate (10 to 25 grammes of the salt). Finally, the liquid is heated and filtered, and the acids liberated by means of hydrochloric acid, and eventually pressed through linen and thoroughly extracted with petroleum spirit, in which the hydroxy derivatives are insoluble.

The yield by this method, however, is considerably less than in Hazura's method. From tallow, about 10 per cent. of hydroxy derivatives were obtained, melting at 126° C. (137° C., *Hazura*).

In order to detect linolic acid, *Fahrion* states that it is sufficient to boil the precipitate with a litre of water instead of extracting it with petroleum spirit. The filtrate from the boiling solution is concentrated to 150 c.c., acidified with hydrochloric acid, and shaken with ether. When sativic acid is present, a white flocculent precipitate will be observed in the ether. In one experiment *Fahrion* thus obtained 0·6 gramme of hydroxy acid, which, after re-crystallisation, melted at 152° C. (*Hazura*, 173° C.).

As regards this discrepancy in the melting points of the hydroxy acids respectively obtained by *Hazura* and by *Fahrion*, *Farnsteiner*[1] is of the opinion that Hazura's substance melting at 160° to 162° C. was not pure sativic acid, but contained traces of an isomeric substance. He also attributes the failure of Benedikt and Hazura to detect more unsaturated fatty acids in lard to the fact that the liquid fatty acids used by them contained too much oleic acid, which interfered with the test for linolic acid. In his experiments he made use of the more unsaturated fatty acids concentrated by treatment of the barium salts with benzene and alcohol as described above (see *Determination of Oleic Acid*).

IV. Determination of Hydroxy Acids.

Treatment of the Fatty Acids with Petroleum Spirit.—*Fahrion*[2] devised the following method for the examination of boiled linseed oil:—From 3 to 5 grammes of the fat are saponified with 15 to 25 c.c. of an 8 per cent. solution of alcoholic sodium hydroxide, the alcohol evaporated, and the soap dissolved in 50 to 70 c.c. of hot water; the solution was decomposed with dilute hydrochloric acid in a large separating funnel, and shaken, when cold, with 100 c.c. of a petroleum spirit (completely volatile below 80° C.). After standing for about an hour, the lower aqueous layer was run off. The hydroxy fatty acids are insoluble in the petroleum spirit, which can be poured off, leaving them adhering to the sides of the funnel. They are washed several times, with petroleum spirit, and dissolved in a little hot alcohol, which is evaporated in a weighed basin, and the residue dried for an hour at 100° to 105° C., and weighed. In this way *Fahrion* found from 0·6 to 31·6 per cent. of insoluble hydroxy acids in different sorts of boiled linseed oil. Usually they were in the form of a thick dark red oil, which was completely soluble in alcohol and ether.

Lewkowitsch[3] found that this method was not generally applicable to hydroxy acids, for pure hydroxystearic acid is slightly soluble in petroleum spirit, and the fatty acids of castor oil behave like the oil itself in being soluble in their own volume of that solvent. He was unable to effect any separation of oleic acid and castor oil fatty acids in this way.

In a further study of this subject,[4] *Lewkowitsch* has proposed the term "oxidised acids" for these insoluble fatty acids. Assuming them to be hydroxy acids with the molecular weight of 300 (hydroxystearic acid, $C_{18}H_{35}(OH)O_2$), it would be possible to calculate their amount by multiplying the acetyl value by 0·55. But, except in the case of commercial blown oils, the calculated results were very different from the weight of the insoluble acids, although parallel therewith. This is shown by the following examples, selected from a long table given by *Lewkowitsch*:—

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[1] *Zeit. Untersuch. Nahr. Genussm.*, 1899, ii., 1-27.

[2] *Zeit, angew. Chem.*, 1891, 540.

[3] *Oils, Fats, and Waxes* (1898), 204.

[4] *Analyst*, 1899, xxiv., 323.

Oil.	Oxidised Acids.	True Acetyl Value.	Acetyl Value × 8·55.
	Per cent.		
Linseed,	..	11·7	6·4
,, blown, 10 hours,	7·1	31·7	17·4
Cotton-seed, blown at 120° C.,	1·28	30·84	16·96
Oleic acid, blown, 4 hours,	6·0	19·4	10·67
Blown rape, commercial,	24·95	53·14	29·22
,, cotton-seed, commercial,	26·45	48·54	26·7
Boiled oil, commercial,	6·5	24·0	13·2

According to *Lewkowitsch,* it is possible to separate "oxidised acids" from hydroxylated acids by taking advantage of the difference in solubility of their salts. He concludes that these "oxidised acids" contain lactonic substances.

Calculation from Increase of Weight on Acetylation.—*Lewkowitsch* [1] has shown that an approximate determination of the hydroxy fatty acids in a fat may be made by boiling the mixed fatty acids with acetic anhydride, washing the product with water and determining the increase in weight, provided the nature of the fatty acids be known. The formula for the calculation is :—

$$y = \frac{100\ Mi}{A\ .\ 42};$$

where M represents the molecular weight of monohydroxy acid, i the increase in weight of A grammes, and y the required percentage of hydroxy acids.

Or, if the hydroxy acid contain n hydroxy groups, the formula will be

$$y = \frac{100\ Mi}{A\ .\ n\ .\ 42},$$

the number 42 being the molecular weight of the acetyl group (C_2H_2O).

Calculation from the Acetyl Value.—*Lewkowitsch* [2] gives the following formula for calculating the percentage of fatty acids from their acetyl value, if their molecular weight be known :—

$$x = \frac{100\ .\ c\ .\ M\ (M + 42)}{56{,}100\ (M - 42)};$$

where x represents the required percentage, M the molecular weight of a hydroxy acid requiring 56,100 milligrammes of potassium hydroxide for neutralisation, and c the observed acetyl value.

An outline of the conclusions arrived at by *Lewkowitsch* as to the meaning of the acetyl value in the analysis of fats is given in Chap. VIII. (*Acetyl Value*).

Magnesium Methyl Iodide Method.—*Zererewitinoff* [3] has based a method of estimating hydroxy fatty acids in fats upon the reaction

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[1] *J. Soc. Chem. Ind.*, 1892, xi., 138.

[2] *Oils, Fats, and Waxes.*

[3] *Zeit. anal. Chem.*, 1913, li., 729.

which takes place between the hydroxy groups and magnesium methyl iodide—

$$CH_3MgI + ROH = CH_4 + RO\,MgI.$$

The carboxyl (—COOH) groups of fatty acids also react, so that allowance has to be made for this in the calculation. In making an estimation the hydroxyl groups present as carboxyl are first determined by titrating a weighed quantity of the fatty acid with alcoholic potassium hydroxide solution:—

$$\text{Per cent. OH} = \frac{17 \times T \times n \times 100}{56 \times a} = 30{\cdot}357\frac{T \times n}{a},$$

where 17 represents the molecular weight of hydroxyl, 56 that of potassium hydroxide, T the titre of the alkali solution, n the number of c.c. used in the titration, and a the weight of the fatty acid.

The total hydroxyl value is then determined by dissolving about 0·2 gramme of the fatty acid in 15 c.c. of anhydrous pyridine in a gas evolution flask connected with a water-jacketed Lunge's nitrometer. About 5 c.c. of magnesium methyl iodide is introduced in a reagent bulb, and after equalisation of temperature the pressure is adjusted, and the liquids mixed. When the evolution of gas has stopped the flask is at once cooled, and the volume of methane measured in the usual way.

The total hydroxyl value is then calculated by means of the formula—

$$\text{Per cent. OH} = \frac{0{\cdot}000719 \times V \times 17 \times 100}{16 \times S} = 0{\cdot}0764\frac{V}{S},$$

where 0·000719 is the weight of 1 c.c. of methane at 0° C. and 760 mm. pressure; 16, the molecular weight of methane; 17, that of hydroxyl, V the volume of methane at 0° C. and 760 mm.; and S the weight of fatty acid.

The difference between the two results gives the hydroxyl value of the fatty acid, which should agree with that calculated by the acetyl method (*q.v.*).

V. Determination of Lactones.

For the determination of lactonic substances, such as the stearolactone formed by the action of sulphuric acid upon oleic acid, *Benedikt* devised a volumetric and a gravimetric method (see Chap. VIII.).

FREE FATTY ACIDS IN NATURAL OILS AND FATS.

Owing to the presence of mucilaginous, albuminous, or gelatinous matters in most crude vegetable oils expressed from seeds, or animal fats and oils obtained from animal tissues, it generally happens that a perceptible amount of hydrolysis of glycerides is brought about in the process of extraction, due to the influence of these substances and the fermentative changes rapidly undergone by them. Even when solvents (such as light petroleum oil, carbon bisulphide, or ether) are used for the isolation of the oil, etc., it not infrequently happens that measurable amounts of free fatty acids are contained in the product obtained. This leads to the conclusion that hydrolytic actions naturally take place in the seeds, tissues, etc., during crushing and analogous operations, or even on simply keeping, so that small quantities of free acids are practically always present in the natural products as obtained on a manufacturing scale from the animal after death, or from the seed after detaching from the plant, even when not normally present in the living animal or growing vegetable.

The extent to which actions of this sort take place is extremely variable; in general the "cold-drawn" oils expressed from seeds, and the corresponding first runnings from fresh fish livers, and the more liquid "oleomargarine" obtained by the action of gentle heat on animal fats, contain much smaller proportions of free fatty acids than the later fractions obtained by subsequent hot pressing and analogous operations; whilst in the case of vegetable oils the maximum amounts of free fatty acids are contained in the oils extracted by solvents from oil-cakes, and in those obtained from vegetable pulps (pounded nuts, crushed olives, and such like) by heating with water so that oily matter floats to the surface and can be separated by skimming—*i.e.*, in those cases where contact with fermentible matters has been most intimate and prolonged. Thus, the following figures were obtained by Noerdlinger,[1] the total fatty matter being extracted from the seeds by means of light petroleum spirit, and the free fatty acid (determined by titration, with phenol-phthalein as indicator) reckoned as oleic acid (*vide infra*):—

Oils.	100 Parts contain		Free Fatty Acids Reckoned per 100 of Total Fat.
	Free Fatty Acids.	Total Fat.	
Rape (*Brassica rapa*),	0·42	37·75	1·10
Cabbage (*B. campestris*),	0·32	41·22	0·77
Poppy (*Papaver somniferum*),	3·20	46·90	6·66
Earth-nut (*Arachis hypogæa*) seed,	1·91	46·09	4·15
Earth-nut (*Arachis hypogæa*) outside pale husk,	1·91	4·43	43·10
Sesamé (*Sesamum orientale*),	2·21	51·59	4·59
Castor (*Ricinus communis*),	1·21	46·32	2·52
Palm-nut (*Elæis guineensis*) containing 6 per cent. husks,	4·19	49·16	8·53
Coconut (*Cocos nucifera*),	2·98	67·40	4·42
Oil Cakes.			
Rape,	0·93	8·81	10·55
Poppy,	5·66	9·63	58·89
Earth-nut,	1·42	7·65	18·62
Sesamé,	6·15	15·44	40·29
Palm-nut,	1·47	10·39	14·28
Coconut,	1·31	13·11	10·51
Linseed,	0·75	8·81	9·75
Castor,	1·27	6·53	20·07

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[1] *J. Soc. Chem. Ind.*, 1890, ix., 422; from *Zeit. anal. Chem.*, xxix., 6.

Obviously, when oil contains any considerable quantity of free fatty acids the use of alkaline refining processes (Chap. XI.) is apt to lead to a considerable diminution in the quantity of refined product obtained, as compared with the raw material employed, because the free fatty acids are removed in the form of soaps, the production of which, moreover, often leads to further loss by the mechanical entangling of "neutral" oil in the saponaceous "foots."

Influence of Fatty Acids.—The presence of free fatty acids in any large quantity in most kinds of oils is detrimental to their value, more especially in reference to certain applications. Thus, in the case of lubricating oils, corrosion of bearings, etc., is more apt to be brought about when free fatty acids are present than when the oil is practically free from them; and hence in such cases alkaline-refining processes will often give a superior result, the more so that acid-refining processes are apt to communicate to oil traces of mineral acid, the corrosive action of which is still more marked. This is notably the case with oils intended for wool spinning and analogous purposes. Colza oil containing much free fatty acids burns less freely, and is more apt to char the wick than comparatively neutral oil. On the other hand, the taste of olive oil is said to be considerably improved by the presence therein of small quantities of free acids; whilst largely hydrolysed oils (*huiles tournantes*) are intentionally prepared for certain special purposes in the textile and dyeing industries.

It has also been shown by Wells and Southcombe[1] that in strictly limited amount free fatty acids greatly improve the lubricating power of mineral oils, and that the improvement effected by a small addition of fatty oil to a mineral oil is largely due to the free fatty acid in the fixed oil.

In the case of blubber oils largely consisting of the compound esters of higher monatomic alcohols of the ethylic series, the hydrolytic actions taking place during storage before and after extraction, and while the "rendering" is taking place, lead to another result—viz., that cetylic alcohol and analogous bodies are contained to a large extent in the oils ultimately obtained. Thus from 30 to 40 per cent., and sometimes more, of so-called "unsaponifiable matter" is frequently found to be present in sperm and other blubber oils, chiefly consisting of alcoholiform products of hydrolytic actions of this description. Similar remarks apply to beeswax, and to the various vegetable waxes of analogous constitution; figures are on record, obtained by various analysts, indicating in extreme cases that from a half to two-thirds of the original compound esters have been hydrolysed by reactions of this description, either occurring naturally during storage, or in consequence of the processes adopted in preparing the raw material.

Determination of Free Fatty Acids. Acid Value.

The most accurate process for determining the amount of free acids contained in a given sample of oil or fat, consists in agitating it with

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[1] *J. Soc. Chem. Ind.*, 1920, xxxix., 47R.

warm alcohol, and adding a standard alkaline solution (preferably alcoholic) until a persistent pink coloration appears after continued shaking, phenol-phthalein being the indicator; the temperature must be high enough to render the fat perfectly fluid. Or the oil may be dissolved in cold ether, mixed with a little alcohol, and the solution titrated with standard alcoholic alkali. If the mean equivalent weight of the free fatty acids be known (or assumed) to be E, the proportion of fatty acids in the free state is given by the formula,

$$x = \frac{E \times n}{w} \times 100,$$

where w is the weight in milligrammes of material taken for examination, n the number of c.c. of normal alkali used,[1] and x the weight of free fatty acids contained in 100 parts of substance (*percentage of free fatty acids*). For since 1 c.c. of normal alkali represents E milligrammes of fatty acids, the total weight of acids contained in w milligrammes of substance is $n \times E$ milligrammes, whence 100 parts of substance contain $\frac{E \times n}{w} \times 100$ parts of free fatty acids.

In many instances the value of E is not known accurately, and in such cases it is more convenient to express the amount of fatty acids in terms of the alkali neutralised. This may be done with respect to 100 parts of original substance, thus giving the *percentage* of potassium hydroxide (or sodium hydroxide) neutralised, according to the alkali employed; but a more usual practice is to express the value relatively to 1,000 parts of original substance, potassium hydroxide (caustic potash, KOH, equivalent 56·1), being selected as the alkali, thus giving *the number of milligrammes of potassium hydroxide neutralised*, conveniently referred to as the "free acid neutralisation value," or, more shortly, as the "acid value," and expressed by the value $\frac{n}{w} \times 56{,}100$.[2]

Thus, suppose that 10 grammes (10,000 milligrammes) of palm oil neutralise 8 c.c. of seminormal alkali, equivalent to 4·0 c.c. of normal alkali; since 1 c.c. of normal alkali corresponds with 56·1 milligrammes of KOH, and with 256 milligrammes of palmitic acid (*i.e.*, E = 256), the result may be stated by saying that the "acid value" is $\frac{4{\cdot}0}{10{,}000} \times 56{,}100 = 22{\cdot}44$; or it may be expressed in terms of percentage of palmitic acid by saying that the substance contains free

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[1] If seminormal (or decinormal) alkali be used, the value of n will obviously be $\frac{1}{2}$ (or $\frac{1}{10}$) of the number of c.c. used, and so on.

[2] Since 1 c.c. of normal alkali represents 56·1 milligrammes of KOH, n c.c. represents $n \times 56{\cdot}1$ milligrammes. Then if A be the acid value as above defined,

$$w : n \times 56{\cdot}1 :: 1{,}000 : A$$

$$\text{whence } A = \frac{n}{w} \times 56{,}100.$$

acids jointly equivalent to $\frac{4\cdot0 \times 256}{10{,}000} \times 100 = 10\cdot24$ per cent. of palmitic acid.

When only small quantities of free acid are present, and extremely sharp valuations are desired, somewhat large quantities of material should be taken for the determination; 20 or 25 grammes, or even more. A less accurate method of determining free fatty acids consists in shaking up the oil, etc., with alcohol, allowing the mixture to stand, separating a known fraction of the alcoholic fluid, and titrating it with standard alkali. The result is apt to be somewhat too low on account of the incomplete solution of all free acid by the alcohol.

In some natural oils (*e.g.*, unrefined cotton-seed oil) substances are present of an acid character, although not belonging to the ordinary fatty acid series, but more resembling the acids of pine resin; these substances neutralise alkali (phenol-phthalein being the indicator), and are consequently included in the total of "free fatty acids" determined by titration. Occasionally ordinary rosin (colophony) is intentionally added to oils or the fatty acids thence derived, either as an adulterant or for special reasons—*e.g.*, in the manufacture of some kinds of waggon grease and "yellow" soap. For the methods used in determining the amount of resin present in such cases, *vide* Chap. XXI.

The separation of the free fatty acids from the neutral fat is readily accomplished by adding alcoholic alkali until just neutral to phenolphthalein, diluting with water, and agitating with ether, or better, with light petroleum spirit.[1] The ethereal liquid on evaporation leaves the neutral fatty matter, which can be weighed and further examined as desired. The aqueous liquid is acidulated and shaken with petroleum spirit, etc., whereby the free fatty acids are similarly obtained.

If mucilaginous matter, etc., is also present, the oil may be ground up in a dish with half its weight of solid sodium carbonate and as much water, and dried on the water-bath; the residue is again stirred up with coarsely powdered pumice-stone, and exhausted with ether containing no alcohol, whereby the neutral fat is dissolved out. The residue is exhausted with hot alcohol, and the resulting soap solution evaporated and decomposed by a mineral acid, so as to obtain the free fatty acids, originally present as such, free from the other constituents. Or the fat, etc., may be treated with ether, carbon bisulphide, or other solvent; then by filtering through a weighed filter and washing the insoluble matter thoroughly, the mucilage, etc., is obtained, whilst the filtrate may be evaporated, and the resulting mixture of neutral fat and free fatty acid further examined as required.

Burstyn's Method.—A physical method of approximately determining the amount of free acid contained in oil (more especially olive oil) has been devised by Burstyn[2] for use in cases where titration by

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[1] In presence of alcohol ether is apt to take up into solution small quantities of soap, as well as neutral fat.

[2] *Dingler's polyt. J.*, ccxvii., 314; also *J. Chem. Soc.*, 1876, i., 769.

chemical means is inconvenient or impracticable. 100 c.c. of the oil to be tested are placed in a stoppered cylinder capable of holding 200 c.c. This is then filled up to the mark with alcohol of 88 to 90 per cent., and the whole well shaken, and allowed to stand two or three hours. The alcohol rises, having dissolved out most of the fatty acids together with a minute amount of oil. The increase in its specific gravity is then determined by testing the upper layer with a highly delicate aræometer, a similar cylinder of the original alcohol used being simultaneously examined side by side. By the aid of a table the amount of free fatty acid is calculated from the increase in specific gravity indicated, the table being so constructed as to allow for the solubility in alcohol of the neutral oil, etc. Apart from the error introduced by the possible presence of varying amounts of phytosterol, or other vegetable substances more or less soluble in alcohol, a very slight difference in temperature between the vessels containing the alcoholic oil solution and the pure alcohol used for comparison produces a great effect on the result. The table is usually arranged so as to show the number of "Burstyn degrees" of free acid—*i.e.*, the number of c.c. of normal alkali neutralised by the free acid contained in 100 c.c. of the oil examined. "One degree" consequently represents 0·282 gramme of oleic acid per 100 c.c., or close to 0·3 per cent. by weight.

DETERMINATION OF UNSAPONIFIABLE CONSTITUENTS.

The unsaponifiable substances contained in many oils and fats, to the extent of a few tenths per cent., are most conveniently determined by saponifying the oil with alcoholic alkali, evaporating off the spirit, and dissolving out matters soluble in such solvents as ether, chloroform, carbon bisulphide, light petroleum spirit, etc., either by means of an extraction arrangement, such as the Soxhlet apparatus described in Chap. IX., or by adding water and agitating with the solvent. Ether frequently dissolves a small amount of soap; on the other hand, small quantities of oil often escape saponification, and are thus extracted; so that it is always preferable to boil a second time with alcoholic alkali the residue left on evaporating off the solvent, and repeat the extraction process with the product. The extraction by means of a Soxhlet arrangement is generally facilitated by placing some sand or powdered pumice-stone in the evaporating vessel employed, and rubbing up therewith the residual soap left after evaporating off the alcohol; the solvent thus obtains more easy access to the matters to be dissolved out, and the operation is effected more quickly and thoroughly.

Unsaponifiable Matter in Soap.—In the analysis of soaps similar methods are often employed. The soap to be tested is reduced to thin shavings which are then cautiously dried, first at a comparatively low temperature (50° to 60° C.), later on at steam heat or a little above, so as to drive off all moisture without fusing the mass. The dried shavings, coarsely powdered, are packed in the Soxhlet tube and exhausted with solvent, preferably light petroleum ether. In this way unsaponified fat contained in the soap, cholesterol and analogous substances derived from the oils and fats employed, waxy matter or hydrocarbons (*e.g.*, paraffin oil) added to the soap, or contained in the materials (*e.g.*, in distilled oleins), and similar constituents are all dissolved out, giving a solution, which, on evaporation, leaves a residue that can be further examined, whilst the purified soap is also analysed.

Extraction Apparatus.—The modification of Soxhlet's extraction apparatus described by *Honig* and *Spitz* (Chap. IX.), is often very convenient for dissolving out the unsaponifiable constituents soluble in ether, light petroleum spirit, etc., after heating with excess of alcoholic alkali, evaporating off the spirit, and dissolving in a minimum of water. The use of petroleum spirit is preferable, as although it often dissolves out a little soap (though usually less than ether), this may be readily removed by agitating with a mixture of equal quantities of alcohol and water (50 per cent. spirit), when the petroleum solution free from soap rises to the surface. Moreover, ethereal liquids often form froths that remain permanent without separating properly for many hours or even days, whilst petroleum spirit is less liable to this inconvenience.

In cases where a portion only of the ethereal or other solution is intended to be drawn off, this is readily effected by running the solution and watery fluid into a graduated vessel, into the mouth of which a doubly perforated cork is fitted, with a washbottle-like arrangement of tubes (Fig. 34, *Chattaway*). The upper and lower levels of the ethereal liquid being read off, the cork and tubes are inserted, and air blown in so as to force out some of the ethereal solution into a weighed dish in which it is subsequently evaporated, the quantity thus drawn off being found by withdrawing the tubes and reading off the difference of level of the top of the ether stratum. When sharp results are required, about 90 to 95 per cent. of the ether should thus be withdrawn, and the remainder diluted, say tenfold, by adding more ether.

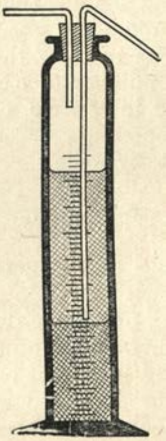
Fig. 34.
Chattaway's Tubes.

The bulk of this is similarly forced out, so that the remaining ether only represents a small percentage of the original ethereal solution.

Thus, suppose that the original ethereal fluid measures 58 c.c., of which 52 are removed by the first blowing out, leaving 6. This is diluted to 60, and another 50 c.c. blown out, leaving 10 of the more dilute liquid, representing 1 of the original solution, or $1 \times \frac{100}{58} =$ 1·72 per cent. Then $100 - 1{\cdot}72 = 98{\cdot}28$ per cent. of the original solution has been blown off, so that the weight of the residue obtained on evaporation of the solution must be increased in the proportion $\frac{58}{57} = \frac{100}{98{\cdot}28}$.

Oils, etc., adulterated with any considerable proportion of hydrocarbons (paraffin, petroleum, rosin oil, etc.), or similar mixtures intentionally prepared for lubricating purposes, etc., are easily separated by the above treatment. When it is required to examine further the fatty acids contained in the saponifiable constituents, they are readily isolated by dissolving in hot water the soap thus freed from hydrocarbons, and adding a mineral acid.

Blubber oils containing the glycerides of higher ethylic alcohols (cetylic alcohol, etc.) when thus treated yield to the solvent the alcoholiform constituents set free during saponification; when these are mixed with hydrocarbons the proportion of alcohol present may be arrived at by means of the hydrogen test (p. 16) or the acetylation test (Chap. VIII.).

When only minute quantities of unsaponifiable matters are contained in a given oil or fat, etc., these are generally either substances akin to cholesterol and phytosterol dissolved in the oil, or else matters of mucilaginous or albuminous character either dissolved in the oil or suspended in a diluted jelly-like form therein. The former, when dissolved out from the soap resulting after saponification by such solvents as ether or petroleum spirit, may often be obtained in a crystallised condition by dissolving in hot alcohol and cooling, or may be converted into benzoic or acetic ethers, etc., and identified either by the melting point or the "acetyl value." The latter are left undissolved; on decomposing the soaps with a mineral acid they form flocculent masses, from which the pure melted fatty acids are readily separable by filtration through a dry paper filter after separation from the aqueous liquor. Some oleaginous matter, extracted by solvents (such as carbon bisulphide) from certain vegetables, seeds, etc., or from certain kinds of animal fatty matter, contain complex bodies of the nature of *lecithin*, a sort of compound ester of choline, glycerophosphoric acid, and fatty acids (oleic and stearic). Phosphorised constituents of this kind are largely contained in the oily matter from the yolks of hens' eggs, and to a less extent in that form the seeds of certain leguminous plants—*e.g.*, peas (*vide infra*).

Methods of Determining Cholesterol and Phytosterol.—Several methods have been devised for the accurate determination of these alcohols as a means of detecting the presence of vegetable oils in animal fats. Cholesterol has been found in appreciable quantities in most of the latter, whilst phytosterol occurs in vegetable oils. The most important of these methods are the following:—

Bömer's Method.[1]—50 grammes of the fat are saponified, and the soap solution diluted with 200 c.c. of water, and shaken for about one minute with 500 c.c. of ether. After standing for a few minutes, the ethereal layer is withdrawn and distilled, and the soap solution extracted two or three times with 200-250 c.c. of ether. The residue from the evaporation of the ethereal extracts may still contain unsaponified fat. This is converted into soap by treatment with 10 c.c. of alcoholic alkali, and the contents of the flask transferred to a separating funnel by means

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[1] *Zeit. Untersuch. Nahr. Genussm.*, 1898, i., 21.

of 20 c.c. of water, and shaken with 80-100 c.c. of ether. The ethereal extract is washed three times with 5-10 c.c. of water, then filtered into a flask, and the solvent slowly evaporated. The residue dried on the water-bath leaves the cholesterol or phytosterol, which can afterwards be purified by crystallisation. When both substances are present, the crystals show only one form, either resembling those of phytosterol or (when cholesterol is present in larger proportion) differing in form from those of ether alcohol.

Von Raumer's Method.—In order to obviate the use of such large quantities of ether, *E. von Raumer*[1] devised the following method :—50 grammes of the fat were saponified with 100 c.c. of alcoholic potassium hydroxide, and the soap solution evaporated to dryness. The residue was powdered, and extracted in a Soxhlet apparatus with 50-75 c.c. of ether. The results obtained showed that a second saponification of the residue in the extractor was unnecessary with careful working.

H. Kreis and *O. Wolf*[2] urged against von Raumer's method that it was difficult completely to dry the soap, and proposed a method based on the extraction of the calcium salts of the fatty acids with strong alcohol, and subsequent extraction of the alcohols with ether.

It was shown, however, that this method did not yield accurate results, and so, eventually, *Kreis* and *Rudin*[3] devised the following modification :—50 grammes of the fat are saponified with 125 c.c. of 95 per cent. alcohol and 25 c.c. of 40 per cent. sodium hydroxide solution, the alcohol evaporated, and the soap dissolved in 500 c.c. of boiling water and precipitated with 100-200 c.c. of a 10 per cent. solution of calcium chloride. When cold, the liquid is filtered through a cotton cloth, and the calcium soap dried between filter paper, finely powdered, and allowed to stand in contact with 100 c.c. of a mixture of equal parts of alcohol and ether for an hour, with frequent agitation. It is then washed on a filter with 100 c.c. of a mixture of equal parts of alcohol and ether, and the filtrate and washings, after evaporation of the ether, mixed with 3 c.c. of a 40 per cent. solution of sodium hydroxide, and evaporated to dryness. The residue is mixed with about 20 grammes of quartz sand and dried on the water-bath, and subsequently for an hour in the hot-water oven. Finally, it is extracted with ether in a Soxhlet apparatus, the ethereal extract evaporated. and the residue recrystallised from alcohol.

In this way cotton-seed oil yielded 0·1480 gramme of phytosterol; butter, 0·1754 gramme of cholesterol; and a lard containing 5 per cent. of cotton-seed oil, 0·0768 gramme of the mixed alcohols.

For the application of this method of extraction to the detection of vegetable oils in lard, see Chap. xv.

Melting Points of Phytosterol and Cholesterol Esters.—*Bömer*[4] gives the following corrected melting points for various esters of cholesterol and phytosterol :—

	Cholesterol.	Phytosterol.
	°C.	°C.
The alcohols themselves, . .	148·4-150·8	138·0-143·8
Formic acid esters, . . .	96·8	105·5-114·3
Acetic acid esters, . . .	114·3-114·8	125·6-137·0
Propionic acid esters, . . .	96·8	106·0-117·3
Butyric acid (normal) esters, .	96·8	86·5- 90·6
Benzoic acid esters, . . .	148·4	145·3-148·4

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[1] *Zeit. angew. Chem.*, 1898, 555.

[2] *Chem. Zeit.*, 1898, xxii., 805.

[3] *Chem. Zeit.*, 1899, xxiii., 986.

[4] *Zeit. Untersuch. Nahr. Genussm.*, 1901, iv., 1070.

Of these esters *Bömer* regards the acetates as the most suitable for his test, which should be employed in conjunction with the ordinary phytosterol test.

The Phytosteryl Acetate Test.—*Bömer*[1] describes the following method of applying his test:—The crude phytosterol or cholesterol obtained from 100 grammes of fat by the method described above is again saponified, treated with ether, the ethereal solution well shaken with water to remove soap, and the residue left on evaporation dissolved in as little alcohol as possible, and allowed to crystallise.

The crystals first separating are examined microscopically, and the alcohol then evaporated, and the residue treated with 2 to 3 c.c. of acetic anhydride, which is heated to the boiling point, and then evaporated on the water-bath. The residue is dissolved in hot absolute alcohol (10 to 25 c.c. for 0·1 to 0·3 gramme of substance), a few additional c.c. of alcohol added to prevent crystallisation, and the clear solution left at the ordinary temperature.

When about half the liquid has evaporated, the crystals are filtered off and recrystallised from 5 to 10 c.c. of absolute alcohol, this process of recrystallisation being continued so long as the material lasts.

The melting point of the crystals is determined after the third and each subsequent crystallisation, and if the temperature of complete fusion is 117° C. (corr.) or higher, *Bömer* regards the presence of vegetable oil as certain.

Vegetable oils containing a large proportion of phytosterol, such as cotton-seed, earth-nut, sesamé, rape, hemp, poppy, and linseed oils, are said to be detected by this test when only present to the extent of 1 to 2 per cent. in animal fats, with the possible exception of egg oil, marine animal oils, and wool fat, which contain large quantities of cholesterol.

In the case of vegetable oils containing less phytosterol—*e.g.*, olive, palm, palm-kernel, and probably coconut oils—from 3 to 5 per cent. can be identified

The test may be made approximately quantitative, when only a small amount of vegetable oil is present, by making comparative tests with mixtures of known composition. As margarine is almost invariably prepared with vegetable oil this test has proved of service in detecting the adulteration of butter with small amounts of margarine.

The following table shows the melting points and optical rotation of the isomeric forms of cholesterol:—[2]

	Melting Point.	Optical Activity.	Authority.
	° C.	$[\alpha]_D$ 15.	
Cholesterol, . . .	145-146	− 36·61	Hesse.
Phytosterol, . . .	132-133	− 34·20	,,
Paracholesterol, . .	134-134·5	− 28·8	Reinke Rodewald.
Caulesterol, . . .	158-159	− 49·60	,, ,,
Isocholesterol, . .	138-138·5	+ 60·00	Schulze.

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[1] *Zeit. Untersuch. Nahr. Genussm.*, 1901, iv., 1070.

[2] Hardin, *J. Amer. Chem. Soc.*, 1899, xxi., 758.

Sitosterol, $C_{27}H_{46}O$ (?), is isomeric with phytosterol, and is present in wheat oil and maize oil. It melts at 138° to 143° C., and has $[\alpha]_D$ 15 $= -23{\cdot}14°$.

Other isomers of cholosterol are *brassicasterol* and *coprosterol*.

The Digitonin Method.—A method of separating cholesterol and phytosterol has been based upon the fact that they combine with digitonin, $C_{55}H_{94}O_{281}$, to form a compound insoluble in water. *Windaus*[1] used an alcoholic solution of digitonin in the test which he applied to the fatty acids from the oil. *Klostermann* and *Opitz*[2] also recommend that the oil should be saponified before the sterols are precipitated, since part of the phytosterol present in vegetable oils is in the form of an ester, which is not precipitated by digitonin.

In a simple modification of the process[3] the free sterols are precipitated by stirring 50 grammes of the melted fat for five minutes at 60° to 70° C. with 20 c.c. of a 1 per cent. alcoholic solution of digitonin, and the mass filtered with the aid of suction, chloroform being added to the hot solution if necessary. The residue of digitonide is washed with six successive portions of 5 c.c. of ether, dried for five minutes at 30° to 40° C., and dissolved in 2 c.c. of hot acetic acid, and the solution boiled for five minutes in a test-tube fitted with a vertical tube to act as a condenser, and then filtered through cotton wool. The tube and filter are washed with two portions (5 c.c. each) of hot absolute alcohol, the filtrate and washings evaporated, and the residue of phytosteryl or cholesteryl acetate examined as described above.

Glycerol.—The methods of determining glycerol in oils, fats, and soaps are described in Chap. XXII.

Presence of Metallic Soaps.—Matters of a saponaceous character are sometimes contained in commercial oils, owing either to the use of basic substances in refining (especially in boiling drying oils), whereby more or less considerable amounts of metallic soaps are formed and partially dissolved by the oil; or to other causes, such as the intentional addition of metallic soaps (aluminium, magnesium, zinc, etc.) for the purpose of increasing the viscosity of lubricating oils; or simultaneous contact with air and metals, whereby a metallic oxide is formed, which then is either dissolved as metallic soap, in virtue of free fatty acids present, or reacts on the glyceride, forming metallic soap by saponification. Oils that have been in contact with copper or brass are often rendered green by the formation of copper soap in this way. Similarly, drying oils that have been "boiled" with metallic oxides as driers (*e.g.*, lead oxide) generally contain more or less metallic soap in solution. Such admixtures, whether intentional or not, can generally be estimated by diluting the oil with ether free from alcohol, filtering, and decomposing the undissolved metallic soap with dilute nitric acid, when the metallic constituents are obtained as nitrates. In most cases prolonged agitation of the oil

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[1] *Zeit. physiol. Chem.*, 1910, lxv., 110.

[2] *Zeit. Nahr. Genussm.*, 1914, xxvii., 713.

[3] Marcusson and Schilling, *Chem. Zeit.*, 1913, xxxvii., 1,001.

with very dilute nitric acid will dissolve out the metallic oxides present as soaps, and in this way it is possible to avoid errors due to the solubility of metallic soaps in the ethereal solution of oil.

Oils containing lead or copper are more or less blackened when shaken with a few drops of hydrogen sulphide water, or a dilute solution of ammonium sulphide. Preferably a mixture of equal volumes of glycerol and water is used to dissolve the sulphur compound employed, as the latter then acts more readily on the oil.

When potassium or sodium soaps are present they can generally be more or less completely extracted by shaking the oils with water, allowing the mixture to stand, separating the aqueous layer, and evaporating it to dryness.

Water contained in Oils, etc.—Although " oil and water " are conventionally regarded as immiscible substances, their mutual insolubility is in most cases relative rather than absolute. Water in general dissolves extremely little oil or fat; but the converse does not hold so closely, as a few tenths per cent. of water can generally be retained in permanent solution by fluid oils, etc., without impairing their transparency. In the case of semi-solid substances (*e.g.*, butter and lard), much larger quantities of water can be mechanically intermixed with the fat in the form of minute globules interspersed throughout the mass; but in this case there is no true solution, and on gently warming the mass so as to melt the fatty matter, the water gradually separates out to the bottom, so that if the operation be effected in a graduated vessel, a reading may subsequently be taken of the volume of water thus separated. In some cases, the separation of the water in this way is facilitated by adding to the mass when just melted a sufficient quantity of light petroleum spirit to prevent it solidifying on cooling, and letting the mixture stand for some time in a stoppered graduated tube, so as to allow the water globules to collect and run together. The amount of water present may also be determined by heating a known weight of substance to a temperature a little above 100° C. (by means of an air-bath or sand-bath), and noting the loss of weight.

When the water actually in solution is to be determined, the same process may be used. Preferably, however, the oil, etc., to be examined is not heated in contact with air, but is placed in a weighed U-tube, through which a current of dry carbon dioxide gas is passed, to prevent oxidation by absorption of oxygen from the atmosphere during the heating.

Adulteration of Fats with Suspended Matters.—Solid and semi-solid fats (lard, tallow, etc.) have been sometimes intentionally adulterated by admixture with white weight-giving substances, such as china-clay, starch, etc. To determine the quantity and nature of the adulterants present in such cases, the fat, etc., is thinned with carbon tetrachloride or other volatile solvent, and filtered through a dry weighed filter. The filtrate and washings being evaporated to dryness, and the residue dried in a steam-bath, the proportion of actual fat present is known. The increase in weight of the filter represents the solid adulterant, and the deficiency in weight the water. The residue on the filter turns blue if starch be present (flour, meal, farina, etc.); cold water dissolves out common salt and such like saline matters (*e.g.*, in salted butters, etc.); kaolin and sand are left behind on incineration; whilst proteins, cellulose, mucilage, and other vegetable non-fatty extractives are burnt off during the process. Oils that have been refined by means of sulphuric acid and retain minute quantities of free inorganic acid, when thus treated with a solvent and filtration, leave on the filter paper a minute amount of residue soluble in water with acid reaction; this may be titrated with decinormal alkali in the usual way.

Constituents containing Sulphur and Phosphorus.—Certain oils, more especially those derived from cruciferous plants (rape, cameline, mustard, horse-radish, cress, etc.), contain small quantities of sulphurised constituents, such as thiocyanic esters. The presence of these may be ascertained by heating the oil with a concentrated solution of potassium hydroxide, whereby potassium sulphide is formed. The mass, after dilution with water and separation of the aqueous liquor, gives a brown or black coloration with an alkaline lead solution. In some cases, heating the oil to "boiling" with a bright strip of silver causes the latter to blacken.

To determine the amount of sulphur, the oil is dissolved in sulphur-free petroleum or alcohol, and burnt in the manner employed in determining sulphur in coal gas, the flame being enclosed in a chimney connected with an aspirator, and absorbing tubes filled with moistened glass beads being interposed, so as to condense sulphur dioxide and trioxide together with the water formed by the combustion. A tray with fragments of solid ammonium carbonate is fixed over the flame, to furnish an ammoniacal atmosphere, and the condensed liquid is oxidised with bromide water, and precipitated with barium chloride and hydrochloric acid (*Allen*).[1]

Or the oil may be cautiously heated with alcoholic potassium hydroxide, evaporated, and the residue incinerated with addition of potassium nitrate till white, the sulphate formed being determined as usual.

This latter method is also available for the estimation of phosphorus present in certain oils and fats as a compound of the nature of lecithin, the phosphorus being ultimately weighed as magnesium pyrophosphate (*Benedikt*).

Jean's Method.[2]—Five grammes of the oil are saponified with 4 c.c. of sodium hydroxide solution (36° B.) and 2 c.c. of alcohol. The mass is dried, the residue dissolved in hot water, and the soap precipitated with sodium chloride. The precipitate is washed with a solution of the same salt, and the sodium sulphide in the filtrate titrated with N/10 iodine solution, of which 1 c.c. = 0·0016 gramme of sulphur.

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[1] *Analyst*, 1888, xiii., 43.

[2] *Ann. de Chim. anal.*, 1901, vi., 321.

GENERAL SCHEME OF EXAMINATION.

The following general scheme for the examination of oils and fats, etc., is applicable in most cases so far as the above-mentioned impurities or constituents are concerned :—

Dry a convenient quantity so as to determine the amount of *water* present.

Melt a known weight of fat and pass it through a hot weighed filter, finally washing out the adherent fat with ether; the residue left on the filter may contain *saline matters, suspended organic impurities, dust*, etc., etc., which may be further examined as occasion requires. On incinerating the filter, the amount of inorganic suspended matter is obtained. Part of the filtered oil, etc., may be shaken successively with water to dissolve out alkaline soapy substances, and with dilute nitric or sulphuric acid in case any lead, copper, or other metallic soaps are present, the aqueous and acid liquid being separated and examined. The oil may advantageously be diluted with ether or carbon tetrachloride, etc., previously to agitation with water, etc.

Another part of the filtered oil is diluted with warm alcohol, and the acid value determined, phenol-phthalein being used as indicator. The alcohol is evaporated and the residue taken up with light petroleum spirit, etc. The residual soap formed from the free acid is examined as required (Chap. XXI.) for fatty acids, resin acids, etc. Aluminium and other metallic soaps, originally present in the oil, may also be found here.

The light petroleum spirit solution on evaporation gives a residue containing neutral oil, hydrocarbons, and unsaponifiable matters, etc. This is saponified with alcoholic alkali, and the product diluted with water and shaken with ether or petroleum spirit. The ethereal solution is evaporated and the treatment with alcoholic alkali repeated to ensure complete saponification. Finally, the hydrocarbons, etc., are dissolved out by means of ether or petroleum spirit, and the aqueous solution of glycerol and fatty acid soaps further examined by acidifying the liquid and separating the fatty acids. These usually constitute 95 to 96 per cent. of the original glycerides (Chap. VIII.).

CHAPTER VII.

CHEMICAL REACTIONS OF OILS, FATS, ETC., AND THEIR USES AS TESTS OF PURITY, ETC.

EFFECT OF HEAT ON OILS, ETC.

When fixed oils, etc., are subjected to heat, decomposition is sooner or later brought about. If the oil be a glyceride, acrolein (acrylic aldehyde, $C_2H_3 . COH$), so named on account of the acrid character of its vapour, is generally evolved. In some cases the fatty acid originally present as glyceride is also volatilised unchanged in greater or less quantity; but in general, destructive distillation only takes place. If the heating be carried out in presence of water vapour, as when superheated steam is blown through the mass, in many cases hydrolysis takes place, fatty acids and glycerol being produced, which more or less completely pass off along with the water vapour. On this action are based certain processes for the manufacture of free fatty acids for candle making, etc., and for preparing pure glycerol.

When drying oils, more especially linseed, poppy, and walnut oils, are heated for the purpose of preparing "boiled" oil for the manufacture of paint, etc., and particularly when the action is pushed to a great length, as in the manufacture of printing ink, the glyceridic portion of the compounds appears to be almost completely decomposed, the linolic acid or anhydride developed being more or less dehydrated (and probably polymerised) in such fashion as to form a highly viscid or rubber-like mass. Oxidation by direct addition of oxygen so as to form hydroxylinolic acid and its derivatives usually occurs simultaneously, more especially in the "blowing" process of preparing boiled oils.

Flash Point.

The determination of the temperature at which inflammable vapours are given off (whether by simple volatilisation, or in consequence of decomposition) in sufficient quantity to take fire by the application of a light to the mixture of air and vapour contained in the upper part of the heating vessel, is a somewhat important operation in the case of many oils intended for lubricating and other purposes, where they are liable to be considerably heated. With animal and vegetable oils the "flash points" are generally high, but much lower numbers are often given by mixtures containing hydrocarbon oils, such as paraffin oil and petroleum distillates, rosin oils, and such like products.

For the determination of the flash point of petroleum distillates and similar substances, several special forms of instrument have been devised by different chemists; in some of the earlier forms the vapour emitted from the warmed oil was allowed free access to the air. This mode of operating was known as the "open test," and was subject to serious irregularities according to the way in which the heating was conducted, and so on.

In the later instruments the top of the heating vessel is closed in to prevent the escape of inflammable vapours when first generated. In consequence a considerably lower temperature is registered by the application of the "close test," whilst the sources of fluctuation in the results are greatly reduced.

Abel's Flash Point Apparatus.—Fig. 35 represents Abel's flash point apparatus, used in Britain as the standard appliance for testing petroleum, etc., under the Petroleum Act. Similar arrangements are in use in other countries, with minor modifications, partly as to the construction of the instrument itself, and partly as to the exact details of manipulation to be observed during use; for as the temperature values deduced are liable to slight fluctuation with variations in the mode of heating, etc., it is essential to adhere strictly to a definite prescribed mode of operating.

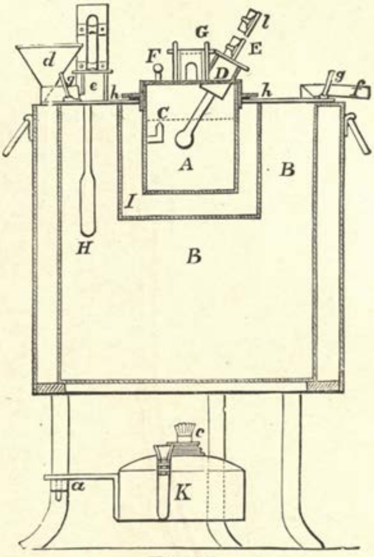

Fig. 35.
Abel's Flash Point Apparatus.

Abel's apparatus consists of a cylindrical metal cup, A, placed inside another with an air-space between, the outer one being surrounded by a water-bath, B, heated by a lamp, K, underneath. The oil to be tested is carefully poured in without splashing until just level with the top of the gauge, C, 1½ inches from the bottom of the cup, the water in the jacket being at the temperature 130° F. (= 54·4° C.), as shown by the thermometer, H. The lid of the cup, D, is then put on, the temperature of the oil being known by means of the thermometer, E. A small lamp, G, is arranged at the top of the cover, swinging on an axis, in such a fashion that when a slide covering an aperture in the lid is drawn aside, the lamp flame is made to pass over the aperture. As the temperature of the contents of the cup slowly rises, the slide is withdrawn at regular intervals of time, governed by the swinging of a pendulum. By and by, the inflammable vapours are given off in sufficient quantity to yield a flash of blue flame by their kindling when the slide is withdrawn; and the temperature then indicated by the thermometer, E, is noted as the flash point. Obviously, this form of apparatus is only suitable for substances the flash point of which is below the temperature of boiling water. When less volatile substances are to be examined, the water jacket is replaced by a hot bath of some other fluid; or a hot-air bath is used instead.

Pensky's Modification.—Fig. 36 indicates Pensky's modification of Abel's instrument for such purposes, in which the source of heat is the lamp flame, C, playing on wire gauze, D, and filling the inverted basin, A, with hot air.[1]

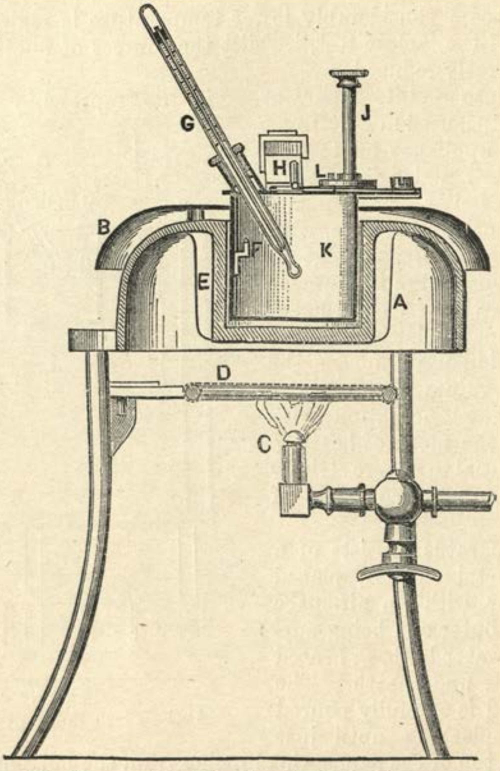

Fig. 36.—Pensky's Modification of Flash Point Apparatus.

Lubricating oils containing hydrocarbons sufficiently volatile to flash at 150° C. or below are distinctly unsafe as regards risk of fire. Animal and vegetable fixed oils (unmixed with hydrocarbons), as a rule, do not flash below 200° to 250° C. Thus *A. Künkler* gives the

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[1] An improved form of Pensky's apparatus has been described by Holde (*J. Soc. Chem. Ind.*, 1889, viii., 734).

following values[1] as the flash points observed with various lubricating fluids, consisting for the most part of petroleum hydrocarbons, and some natural oils, etc. :—

	Sp. Gr. at 17·5° C.	Degrees C.
Cylinder oils—Russian,	0·911-0·923	183-238
,, American,	0·886-0·899	280-283
Machine oils—Russian,	0·893-0·920	138-197
,, American,	0·884-0·920	187-206
Spindle oils—Russian,	0·893-0·895	163-167
,, American,	0·908-0·911	187-200
Rape oil—crude,	0·920	265
,, refined,	0·911	305
Olive oil,	0·914	205
Castor oil,	0·963	275
Linseed oil,	0·930	285
Tallow,	0·951	265

Spontaneous Oxidation of Oils, Fats, etc.

Oils of the drying class, and to a less extent many other oils and fats, possess the property of directly absorbing oxygen from the air at the ordinary temperature, the effect being much more marked when more or less heat is applied. The drying and hardening of paint prepared from linseed oil is an extreme case of such an action, whilst the thickening and "gumming" of various other oils on keeping exhibits the same kind of phenomenon in a less degree. The fixation of oxygen during actions of this kind appears to be principally due to a direct combination of oxygen with acid radicles of "unsaturated" character, precisely analogous to the absorption of iodine or bromine. As the oxidation proceeds, the "iodine absorbing power" of the substance usually diminishes *pari passu*.

In some cases the rapidity with which the absorption of oxygen takes place is greatly enhanced by heating the oil to a temperature insufficient to produce any great degree of decomposition, although high enough to cause incipient breaking-up with evolution of vapours. This process of "boiling" oil in the presence of certain metallic compounds or "driers" appear to consist essentially in the formation of substances that act as "carriers" of oxygen;[2] so that "boiled" oils dry more rapidly than the same oils in a raw or unboiled condition, these carriers absorbing oxygen more rapidly from the air, and parting with it again to the unoxidised portions of the oil.

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[1] *J. Soc. Chem. Ind.*, 1890, 197; from *Dingler's polyt. J.*, cclxxiv., 276.

[2] The rotting of painted canvas sometimes observed appears to be largely due to oxidation of the fibres of the fabric in consequence of this "carrier" action. The presence of certain kinds of resinous matter (such as are employed in the manufacture of tarpaulins, etc.), seems to diminish the tendency to this destructive action.

Amsel stated that boiled oils without an addition of "driers" lost their drying properties, but this is controverted by *Lippert*,[1] who finds that such oils do eventually become dry, though more slowly than those boiled with metallic compounds, and that they yield peculiarly elastic films.

An oil containing manganese salts dries more rapidly in dry air in proportion to the amount of manganese present, but when exposed to moist air the rapidity of drying varies inversely with the proportion of manganese. It is, therefore, advisable to avoid an excess of manganese (*Lippert*[2]). Free exposure to air whilst heating, in some cases accompanied by the injection of a current of air through the heated mass, appears to be essential to the production of the initial degree of oxidation effected in the boiling of drying oils. The latter process when applied to various non-drying oils (more especially fish oils), causes a considerable increase in density and viscidity, so that "blown" oils thus prepared are more suitable for lubricating and other purposes than the original untreated substances.

Effect of Light on Oils.

Exposure to light produces a remarkable increase in the rate at which spontaneous oxidation of oils, etc., takes place at the ordinary temperature. The result of this oxidation is uniformly to cause an increase in specific gravity and in the amount of heat evolved on mixture with sulphuric acid (*infra*), together with a decrease in the iodine absorption (Chap. VIII.). Thus, the following figures were obtained (with many others) by *H. Ballantyne*[3] with olive, castor, rape, cotton-seed, arachis, and linseed oils; specimens kept in the dark for six months showed little or no alteration whether in tightly corked or open bottles, and whether undisturbed or agitated daily so as to aërate them; whereas similar specimens exposed to sunlight during the same period exhibited perceptible amounts of alteration, even when kept undisturbed in corked bottles; and much larger amounts when kept in uncorked bottles and agitated daily:—

Variation in Specific Gravity.

	Original Value, practically Unchanged in the Dark.	Value after Six Months' Exposure to Sunlight.	
		Undisturbed, Corked.	Agitated Daily, Uncorked.
Olive oil, ...	0·9168	0·9185	0·9246
Castor oil, ...	0·9679	...	0·9683
Rape oil, ...	0·9168	0·9171	0·9207
Cotton-seed oil, . . .	0·9225	0·9236	0·9320
Arachis oil, ...	0·9209	0·9216	0·9267
Linseed oil, ...	0·9325	0·9327	0·9385

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[1] *Chem. Zeit.*, 1897, xxi., 175.

[2] *Zeit. angew. Chem.*, 1900, 133.

[3] *J. Soc. Chem. Ind.*, 1891, x., 29.

Variation in Iodine Absorption.

	Original Value, practically Unchanged in the Dark.	Value after Six Months' Exposure to Sunlight.	
		Undisturbed, Corked.	Agitated Daily, Uncorked.
Olive oil,	83·16	82·64	78·24
Castor oil,	83·63	...	83·27
Rape oil,	105·59	105·27	102·12
Cotton-seed oil,	106·84	106·40	100·12
Arachis oil,	98·67	97·60	93·20
Linseed oil,	173·46	172·88	166·17

Only minute amounts of free acid were developed in six months during the course of these observations, indicating but little hydrolysis of glycerides during the oxidation of the insolated samples. The maximum amounts formed in the case of linseed and cotton-seed oils corresponded with a development of 0·34 and 0·50 per cent. respectively of free acid (expressed as oleic acid) in sunlight, none at all being formed in the dark. Olive oil kept for six months in the dark gave a hard solid elaidin; that exposed to sunlight in corked bottles without agitation a somewhat less hard mass; but that insolated and agitated daily, so as to expose it as thoroughly as possible to oxidising influences, did not even thicken when submitted to the elaidin test. Similarly Becchi's silver test for cotton-seed oil gave only faint indications with the insolated oxidised oil, although reacting thoroughly with oil kept in the dark. The viscosity of rape oil, as indicated by the efflux test (*q.v*), was notably increased by nine months' exposure to sunlight (in corked bottles without agitation); oil kept in the dark giving times of flow 56 at 15·5° C. and 25·5 at 50° C., whilst insolated oil gave 66 at 15·5° C. and 26·5 at 50° C. Castor oil, mainly consisting of the glycerides of acids already oxidised, as might *a priori* be expected, is less changed by oxidation than any of the others.

Similar observations have been recorded by various other chemists, the general result of which is to show that the changes brought about in oils and fats by keeping and atmospheric oxidation are greatly accelerated by the influence of light.

RANCIDITY OF FATS.

The term "rancidity" is applied to the alteration which oils and fats undergo when not protected from the influence of air and light. The oils acquire a sharp, disagreeable taste and odour, their proportion of free acids gradually increases, and they undergo various other chemical alterations.

According to *E. Ritsert* rancidity is only produced in oils in presence of oxygen (air), the action being greatly accelerated by simultaneous exposure to light. No effect, however, is produced by the action of light alone, when access of oxygen is entirely excluded.

It was shown by *Ballantyne*[1] that the liberation of free fatty acids was not the cause of rancidity, for in some of his experiments it was found that the oil became rancid prior to the formation of free fatty acids, whilst in other cases the reverse was the case. He was unable to trace any connection between the degree of rancidity and the proportion of free acid.

Spaeth,[2] after a long experimental investigation on lard, arrived at the following conclusions :—

(1) The rancidity of fats is caused by an oxidation process, brought about by the action of air and light. The unsaturated acids are first attacked with the formation of acids containing less carbon, and subsequently aldehydic substances and hydroxy acids are produced.

(2) In the course of oxidation and formation of free acids the amount of volatile acids is considerably increased.

(3) All the fatty acids present contribute to the formation of the free fatty acids.

(4) As the oxidation proceeds the power of absorbing iodine correspondingly decreases, owing to the above-mentioned oxidation and decomposition of the unsaturated fatty acids, and their polymerisation. Fats thus oxidised have a considerably higher refractive index than the normal fats, which must be attributed to polymerisation of the unsaturated fatty acids.

(5) In general, rancid fats show a higher melting point than the fresh fats.

Scala[3] isolated the following compounds from rancid olive oil :—Œnanthylic aldehyde, and formic, acetic, butyric, œnanthylic, azelaic, and sebacic acids. He attributes the disagreeable taste and odour of rancid fats to the œnanthylic aldehyde. Pure palmitic and stearic acids exposed to the influence of air and light for six months did not alter in weight. In comparative experiments with different fats it was found that the greatest increase in weight under these conditions was in the one containing the most fatty anhydride.

Mjoen's[4] experiments confirm the conclusion of other observers as to the rancidity of fats being due to oxidation caused by the action of air and light, and accompanied by the liberation of free fatty acids and decrease in the iodine value. Light, however, is not an essential, although the changes that take place in the absence of sunlight are of a distinctly different character.

In *Mjoen's* opinion, bacteria and moulds have no action upon fresh fats, though they may possibly play some part in subsequent changes when once the decomposition process has commenced.

Brown[5] has studied the effect of rancidity on the chemical and physical characteristics of butter fat. He finds that, with the increase

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[1] *J. Soc. Chem. Ind.*, 1891, x., 29.

[2] *Zeit. anal. Chem.*, 1896, xxxv., 471.

[3] *Staz. sper. agrar. ital.*, 1898, xxx., 613.

[4] *Forschungs Ber.*, 1897, iv., 195.

[5] *J. Amer. Chem. Soc.*, 1899, xxi., 975.

in rancidity, there is a decided increase in the acid, saponification, and acetyl values, and a decrease in the iodine value, and percentage of insoluble fatty acids, and glycerol. The specific gravity is also considerably increased, and there is a slight increase in the melting point. In certain cases phenomena of double melting point (*q.v.*) may be observed in the earlier stages of rancidity, and to this cause Brown attributes the peculiar semi-solid consistency of rancid fats, which he considers is due to the presence of two classes of decomposition products, such as aldehydes and hydroxy acids.

Nagel[1] has identified in rancid fats and oils substances belonging to the following classes of compounds :—(1) Free fatty acids, saturated and unsaturated ; (2) hydroxy fatty acids ; (3) lactones and anhydrides of fatty acids ; (4) alcohols, such as butylic alcohol ; (5) esters of various fatty acids, with higher and, in some cases, polybasic alcohols ; (6) aldehydes, saturated and unsaturated ; (7) acetals, and (8) terpenes.

In examining the fat he removes all the free acids by precipitation with soluble glass (sodium silicate). The lactones can be separated by distillation with steam, or, when not volatile, are converted into hydroxy acids by boiling the oil, after removal of free acids, with a concentrated solution of alkali, and the insoluble salts separated by filtration. Alcohols, esters, and aldehydes, when volatile with steam, are distilled. Non-volatile aldehydes are removed by shaking the oil with one-fourth of its volume of concentrated sodium bisulphite solution, and separating the aqueous layer on cooling. Acetals not volatile with water vapour are best removed after decomposing them into alcohols and aldehydes by treatment with sulphuric acid. Terpenes are distilled over in a current of steam. In order to prevent change during the distillation, the steam can be either accompanied by a neutral gas or superheated gradually (100°-170° C.). In fractionating with superheated steam, the more volatile constituents pass over before the more highly-heated steam, which would decompose them, is introduced. The oil is subsequently cooled *in vacuo*, or in an atmosphere of carbon dioxide or hydrogen.

A method of purifying rancid fats and oils on a large scale is based on this method of separating the several constituents (see Chap. XI.).

There can be but little doubt but that the lipoclastic enzymes present in many vegetable seeds are important factors in the development of rancidity, and for this reason such fats as palm-kernel oil and coconut oil should be expressed as soon as possible after gathering.

Detection of Rancidity.—In order to detect the presence of rancidity in fats when not indicated by the acidity, *Kreis*[2] suggests the use of Bishop's reaction for sesamé oil (*q.v.*). The green colour is not given by fresh sesamé oil, but is at once obtained on the addition of a small quantity of a rancid oil or fat, or after exposure of the sesamé oil itself for some days to the action of air and sunlight.

The Oxidisability Value.—*Issoglio*[3] has based a method of estimating the degree of rancidity of fats upon the measurement of the proportion of aldehydes, etc., distilled from the fat in a current of steam under constant conditions. From 20 to 25 grammes of the sample are mixed

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[1] *Amer. Chem. J.*, 1900, xxiii., 173.

[2] *Chem. Zeit.*, 1899, xxiii., 802.

[3] *Annali Chim. Applic.*, 1916, vi., 1.

with 100 c.c. of water and distilled in a current of steam, so that 100 c.c. of the distillate are collected in ten minutes. Ten c.c. of the distillate are mixed with 50 c.c. of water, 10 c.c. of 20 per cent. sulphuric acid, and 50 c.c. of $\frac{N}{100}$ potassium permanganate solution, and the mixture boiled for five minutes in a flask connected with a ground-in condenser. After cooling, the liquid is treated with 50 c.c. of $\frac{N}{100}$ oxalic acid solution, and titrated with $\frac{N}{100}$ potassium permanganate solution. If N represents the amount of permanganate required for the oxidation, and n that required in a blank test, and P the weight of fat taken, the *oxidisability value* of the fat may be expressed by the equation—

$$x = \frac{(N - n)\,80}{P}.$$

Hence this value represents the milligrammes of oxgyen required to oxidise the organic compounds separated under constant conditions from the fat.

As a rule the oxidisability value of sound fresh fats ranges from about 3 to 10, whilst rancid fats show much higher values. The acid value does not stand in any definite relationship to the oxidisability value. For example, fifteen samples of fresh, sound olive oils of different origin gave acid values ranging from 1·88 to 8·59 and oxidisability values of 3·20 to 10·45, whilst six samples of rancid olive oil showed acid values of 6·51 to 18·56 and oxidisability values of 14·62 to 59·10.

Biochemical Test for Rancidity.—*Vintilesco* and *Popesco*[1] have shown that fats in becoming rancid absorb oxygen, and can then take the place of hydrogen peroxide or oxidised oil of turpentine in the peroxydase test for blood :—About 10 grammes of the oil or melted fat are mixed with 4 to 5 drops of an aqueous solution of blood or of 3 per cent. hæmoglobin solution, 10 drops of freshly-prepared guaiacum tincture, and about 10 c.c. of water, and the tube closed and vigorously shaken for a minute. In the case of sound fats no coloration is produced, but rancid fats cause a blue coloration to appear, the intensity of which is proportional to the degree of oxidation. In the case of slight rancidity the coloration is rendered more apparent by shaking the mixture with an equal volume of 95 per cent. alcohol, in which the oxidation product is soluble. Rancid fats give the reaction after heating for a few minutes at 120° C., but not after heating at 200° C.

Spontaneous Combustion.

When a film of readily oxidisable oil is spread over a considerable surface, so that a large area is presented for atmospheric oxidation, if the circumstances are such that the heat generated by the action is not readily lost, the mass becomes greatly heated, in some cases to

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[1] *J. Pharm. Chim.*, 1915, xii., 318.

such an extent as to bring about spontaneous inflammation. *Gellatly* has shown that greasy cotton rags and similar materials kept in a warm place are, in consequence, liable to ignite spontaneously, and are accordingly a source of danger as regards fire. Boiled linseed oil appears to be the most energetic of oils in this respect. A handful of cotton waste soaked in this fluid and squeezed out, and then kept in a box at 70° to 80° C. soon rises greatly in temperature to nearly 200° C.; and in little more than an hour the mass is so hot that smoke issues, and on opening the box the whole takes fire. Unboiled linseed oil takes a much longer time to produce the same result[1] (from one to six hours), and rape oil longer still (some ten hours). On the other hand, an admixture of mineral oil greatly retards the action. In general, the greater the iodine absorption of the oil, the greater the tendency to spontaneous oxidation.

Allbright & Clark's Apparatus.—A testing apparatus has been constructed by *Allbright & Clark*[2] for determining the comparative liability of oils to spontaneous combustion. This consists of an outer shell formed by a 6-inch wrought-iron tube which can be closed at each end by discs of wood. Inserted into this tube is an inner 4-inch sheet-iron tube with overlapping metal covers at each end, so that an air-space is left of 1 inch around the inner tube, and of 3 inches at each end. Three thermometers are inserted into the inner shell through the outer one. A ball of, say, 50 grammes of waste, over which an equal weight of oil is distributed, is carefully pushed to one end of the inner tube, and the corresponding thermometer bulb inserted into the middle of the ball. A similar ball of unoiled waste is placed at the other end, with another thermometer bulb inserted as before. The third thermometer is placed between the two. On heating the outer tube by means of a Bunsen burner, so that the central thermometer indicates about 125°, the temperature of the unoiled waste ball will be about 100°. That of the other rises in proportion as the oil oxidises more rapidly.

Richards[3] found that this arrangement gave most valuable results in gauging the degree of safety of lubricating oils, etc. For instance, the percentage of fatty oil which may be safely mixed with mineral oils may be determined in this way. Thus, neat's foot oil and best lard oil may be added to the extent of 50 to 60 per cent., whilst not more than 25 per cent. of cotton-seed oil is permissible.

Mackey[4] has shown that the free fatty acids obtained from cotton-seed oil and olive oil are more liable to develop heat when spread upon cotton waste than the oils themselves, and that this point has a considerable bearing on insurance risks, seeing that a large proportion of free fatty acids is present in recovered cloth oils and distilled oils.

Mackey's Method.—In a later communication[5] *Mackey* gives a

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[1] Renouard (*J. Soc. Chem. Ind.*, 1882, i., 184) repeated these experiments and confirmed this difference between boiled and raw linseed oil.

[2] *J. Soc. Chem. Ind.*, 1892, xi., 547.

[3] *J. Soc. Chem. Ind.*, 1892, xi., 547.

[4] *J. Soc. Chem. Ind.*, 1894, xiii., 1164.

[5] *J. Soc. Chem. Ind.*, 1895, xiv., 940.

description of an apparatus devised for testing oils. It consists of a piece of wire gauze 5 inches square (24 meshes to the inch), which is tied with copper wire into a roll, the ends of which overlap. Into this roll are introduced 7 grammes of cotton-wool previously soaked in 14 grammes of the oil, and the roll is now placed in a closed water-oven, the water of which is boiling. A thermometer is passed through a cork fitted into the opening of the oven, and its bulb is inserted into the centre of the wool. The temperature is then taken at stated intervals. The following representative examples illustrate this method :—

Oil Examined.	Temperature in 1 Hour.	Temperature in 1½ Hours.	Temperature in 2 Hours.	Maximum Temperature.	
	°C.	°C.	°C.	°C.	Hr. M.
Cotton-seed oil fatty acids,	151	215	..	215	in 1 25
Olive oil fatty acids,	104	210	..	335	„ 1 50
Cotton-seed oil,	105	228	..	228	„ 1 25
Olive oil,	96	97·5	97·5	102	„ 4 15
Oleine,	94·5	96	97·5	105·5	„ 5 15

Mackey regards all oils which either take fire or reach a temperature of over 200° C. in less than two hours as dangerous. He also shows by this test that an addition of mineral oil to a glyceridic oil diminishes the risk of spontaneous combustion.

The chief objection to this test is that the quantities used are too small, and that the conditions are not parallel with those that obtain when oily cotton waste is exposed to the air in mass.

MEASUREMENT OF OXYGEN ABSORPTION.

Film-test.—If a film of oil be freely exposed to the air, so that heating to any considerable extent is impracticable, the effect of the oxidation is gradually to thicken the oil, and finally to convert it into a varnish-like product. A test of the quality of a given sample of drying oil is based upon this, a glass plate being coated on one side with a film of oil, after the fashion of a photographer's collodion plate, and then kept in a steam-bath for some hours, preferably side by side with another plate similarly coated with oil of standard quality. The relative length of time requisite before the film ceases to be "tacky," being converted into a dry varnish, serves as a measure of its drying quality. Thus, whilst a good sample of linseed oil is completely solidified in some twelve hours, non-drying oils like arachis and olive oils are scarcely thickened at all; whilst cotton-seed oil and similar substances possessing only a certain degree of drying power are intermediate. In this respect the order in which vegetable oils are arranged by means of this test is approximately the same as that in which they are arranged by means of the iodine absorption reaction (Chap. VIII.).

Kissling[1] obtained the following results by exposing for ten days 10 grammes of the different oils spread over a surface of 35 sq. cm., and then determining the increase of weight :—

Oil.	Gain in Weight per cent.
Olive oil, ...	0·0
Rape oil, crude, ...	0·05
Neat's-foot oil, refined, . . .	0·065
Cotton-seed oil, ...	0·545
Linseed oil, crude, ...	1·130
„ boiled, ...	3·400

At higher temperature (100° to 105° C.) rape oil showed a slight increase in weight (0·42 to 1·08 per cent.) after twenty-two hours.

In *Lippert's*[2] opinion Kissling's first experiments showed too small an absorption of oxygen, owing to the excessive depth of the oil. *Lippert* finds, however, that within certain limits a film on a plate is not influenced by the thickness. In his experiments raw linseed increased slowly in weight for three days, more rapidly on the fourth day, and was dry on the seventh day. He considers it inadvisable to expel the condensed moisture at 80° C., owing to the possibility of anhydrides being formed. Linseed oil boiled without " driers " absorbs oxygen more slowly than raw oil, but eventually the increase in weight is within 2 per cent. of that gained by the raw oil. He suggests that the speed of drying shall be taken as the time required to attain the maximum increase in weight.

Influence of Driers.—*Lippert*[3] found that boiled oil containing manganese resinate remained " tacky " during the whole time it was gaining in weight. The best results were obtained when the oil contained 0·15 per cent. of manganese. The dried film from a varnish containing 0·2 per cent. of manganese resinate became soft and sticky again after standing for four weeks.

In the case of litharge varnishes, prepared by dissolving 0·34 to 6·8 per cent. of litharge in linseed oil heated to 220°-230° C., all the films were hard when the maximum increase of weight was attained, but became soft again on standing, especially when the proportion of the metallic compound was high. Hence, softening of the film cannot be taken as a proof of the presence of rosin or rosin oil.

When a boiled oil contains either of the latter substances the amount of oxygen that it can absorb depends to a large extent upon the proportion of " drier " present, though an absorption of less than 12 per cent. usually points to adulteration.

The following table shows the maximum increase in weight of a

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[1] Abst. *J. Soc. Chem. Ind.*, 1891, x., 778.

[2] *Zeit. angew. Chem.*, 1898, 412.

[3] *Zeit. angew. Chem.*, 1898, 431.

manganese varnish containing different quantities of rosin oil and colophony :—

MnO Varnish Adulterated with	Increase in Weight Per Cent.		
	I.	II.	III.
Rosin oil, 5 per cent.,	10·09	11·14	7·31
,, 15 ,,	8·63	10·09	11·35
,, 25 ,,	7·46	10·13	11·23
Colophony, 5 ,,	7·86	7·01	11·73
,, 15 ,,	7·08	7·20	10·21
,, 25 ,,	9·53	10·07	11·06

Any considerable proportion of colophony or rosin oil will produce "tackiness" after the film has begun to lose in weight, whilst lack of "driers" is indicated by reduced speed in drying.

Gawalowski[1] adopts the following method :—From 5 to 8 grammes of the oil are spread over a thin strip of platinum foil, which is then bent into a spiral, and placed in a drying tube, the ends of which are closed by platinised asbestos. A current of dry air, freed from carbon dioxide, is passed through the tube for about three weeks, the moisture and carbon dioxide evolved collected in the ordinary absorption tubes, and the tube and spiral finally weighed.

Mannhardt[2] uses a frame containing aluminium plates for the test. From 0·5 to 0·7 gramme of the oil is distributed over the plates by means of the finger, and a control test with a standard oil is made simultaneously. To obtain trustworthy results, the comparative tests are always made under definite conditions of moisture in the atmosphere, etc., with free access of air, and under the same degree of illumination.

Livache's Test.—*Livache*[3] found that the rate of absorption of oxygen was much quickened if finely-divided metallic lead were mixed with the oil to be examined. Comparative tests are readily made by placing on a watchglass about a gramme of lead[4] in a thin layer, and then dropping on to it a few decigrammes (not more than 6 or 7) of oil in small drops, scattered over different portions of the lead, so as not to run into one another. The whole is then weighed and allowed to stand at the ordinary temperature.

Drying oils begin to increase measurably in weight in less than twenty-four hours, and cease to gain weight after three to six days, whilst oils possessing little or no drying qualities do not increase at all for several days. Similar remarks apply to the fatty acids isolated from the oils. Thus, the following figures were obtained :—

[1] *Chem. Rev. Fett Ind.*, 1898, v., 9.

[2] *J. Ind. Eng. Chem.*, 1913, v., 129.

[3] Abst. *J. Soc. Chem. Ind.*, 1886, v., 494.

[4] Precipitated from lead acetate solution by means of zinc, and rapidly washed with water, alcohol, and ether in succession, and finally dried *in vacuo*.

	Percentage Increase in Weight		
	Of Oil after		Of Fatty Acids after 8 Days.
	2 Days.	7 Days.	
Linseed oil,	14·3	...	11·0
Nut oil,	7·9	...	6·0
Poppy oil,	6·8	...	3·7
Cotton-seed oil,	5·9	...	0·8
Beech-mast oil,	4·3	...	2·6
Colza oil,	Nil.	2·9	2·6
Arachis oil,	,,	1·8	1·3
Rape oil,	,,	2·9	0·9
Olive oil,	,,	1·7	0·7
Sesamé oil,	,,	2·4	2·0

According to *Hübl* precipitated copper is preferable to lead, and this view is also taken by *Lippert*,[1] who finds by experiment that Livache's method is not a suitable means of determining the value of drying oils for the manufacture of varnish. His results show that the use of copper powder yields figures in closer agreement with the film test.

A modification of *Livache's* method has been devised by *Liverseege* and *Elsdon*,[2] in which a layer of dried powdered litharge is mixed with about 0·7 gramme of the oil in a basin of German silver. After weighing the basin and its contents 5 c.c. of methylated ether are added, and the basin rotated to mix the moist mass, and then placed in an incubator for two or three days until the maximum weight is attained (see *Linseed oil*).

Gas-Volumetric Method.—*Bach*, following *Fresenius*, tests the oxygen-absorbing power of oils by heating them in a closed tube containing oxygen, and noting the volume of gas absorbed. The presence of excess of oxygen after the experiment must be proved by means of a glowing splinter of wood. This test is more particularly useful in the valuation of certain kinds of lubricating oils (see *Analysis of Lubricants*, Chap. XIV.). This method was also used by *Fox* prior to *Bach*, and a similar method has been devised by *Wilson* and *Heaven*.[3]

Fahrion's Method.—*Vogel* suggested the use of cotton-wool as an absorbent for the oil, but *Fahrion*[4] found that soft porous chamois leather was preferable. Strips weighing about 1 gramme were made to absorb an equal weight of oil and suspended from brass hooks, whilst simultaneously blank tests were made with similar strips of the same leather, so as to eliminate the effect of atmospheric moisture. In

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[1] *Chem. Rev. Fett Ind.*, 1899, vi., 65.

[2] *J. Soc. Chem. Ind.*, 1912, xxxi., 207.

[3] *Ibid.*, 565.

[4] *Chem. Zeit.*, 1894, xvii., 1453; *J. Soc. Chem. Ind.*, 1894, xiii., 405.

most cases, the amount of oxygen absorbed did not correspond with the theoretical oxygen absorption as calculated from the iodine value. The percentage increase in weight of the different oils from day to day is shown in the following table :—

	Leather.	Olive Oil.	Sesamé Oil.	Colza Oil.	Cotton-seed Oil.	Poppy Oil.	Nut Oil.	Linseed Oil.	Cod-liver Oil.
Iodine value, .	...	82·1	110·2	102·4	109·2	135·9	149·2	175·8	171·0
After 1 day, .	0	0·2	0·1	0·1	−0·1	0·3	−0·2	0·1	−0·6
,, 2 days, .	1·0	1·0	1·2	1·1	0·8	2·0	2·0	1·5	1·1
,, 3 ,, .	1·3	1·2	0·9	1·3	1·4	3·2	4·4	2·0	8·1
,, 4 ,, .	0·9	0·9	0·5	1·0	1·2	4·3	7·1	3·8	10·0
,, 5 ,, .	1·4	1·4	1·1	1·8	3·1	7·1	9·7	12·3	10·9
,, 6 ,, .	−0·6	−0·4	−0·5	0·5	2·2	7·3	8·4	11·8	8·0
,, 7 ,, .	1·3	1·1	1·0	2·5	5·0	9·7	9·6	13·2	10·4
,, 8 ,, .	0	−0·1	0	2·0	4·7	7·0	7·2	10·4	8·0
,, 9 ,, .	0·5	0·5	0·7	2·8	5·7	7·3	7·3	11·3	8·5
,, 10 ,, .	1·8	1·7	2·0	4·6	7·4	8·0	8·3	11·8	10·1
,, 14 ,, .	−0·5	−0·4	1·1	2·3	2·5	3·3	4·0	7·9	6·8
,, 3 weeks,	1·1	0·7	4·7	3·2	1·6	2·7	4·2	8·2	6·3
,, 4 ,, .	3·3	3·5	6·6	6·3	5·2	6·7	8·4	12·6	11·8
,, 6 ,, .	−2·5	−2·5	−0·5	−0·2	−1·4	−0·3	−1·3	4·5	4·3
Maximum, .	...	0·2	3·6	2·8	5·6	8·4	9·0	12·4	9·5
Livache's test,	...	1·7	2·4	2·9	5·9	6·8	7·9	14·3	6·4
Calculated absorption, .	...	5·2	7·0	6·5	6·9	8·6	9·4	11·1	10·0

Bishop's Manganese Resinate Method.—In order to accelerate the drying process still more *Bishop*[1] mixes the oil with precipitated silica and manganese resinate to act as an oxygen carrier. The manganese resinate is purified by treating the commercial product with ether or petroleum spirit, filtering, and evaporating the filtrate. The dry residue, which *Bishop* found to contain 9·8 per cent. of manganese oxide, is kept in a stoppered bottle.

For the determination of the oxygen absorption, from 5 to 10 grammes of the oil are heated in a dish on the water-bath with 2 per cent. of the manganese resinate, the mass being continually stirred until solution is complete. One gramme of silica is then weighed into a flat dish provided with a stirring-rod, and then drop by drop from a pipette 1·02 gramme of the resinated oil (1 gramme of oil + 0·02 gramme of resinate) is added. The well-mixed mass is spread over the bottom of the dish, which is then kept at a temperature of 17° to 25° C. for drying oils, and 20° to 23° C. for other oils. The dish is weighed after six hours and twice again in the twenty-four hours, and so on, until its weight no longer increases. The maximum increase in weight multiplied by 100 gives the oxidation figure.

The subjoined table gives a general summary of the results thus obtained by *Bishop*. These show that arachis oil occupies an intermediate position between the semi-drying oils like cotton-seed oil, and

[1] *J. Pharm. Chim.*, 1896, 55.

the non-drying oils like colza and olive oil. In the case of the latter a somewhat higher temperature (20° to 30° C.) is advisable, and even then the oxidation is not complete in a short time :—

Oil.	Specific Gravity.	Degree of Oxidation.	Mean Degree.
Linseed, French, . . .	0·9227	17·70-16·40	17·05
,, La Plata, . .	0·9304	15·45-15·00	15·20
Hemp-seed, ...	0·9287	14·55-14·30	14·40
Poppy, French, . . .	0·924	14·50-13·90	14·20
Nut, ...	0·924	13·70	13·70
Cotton-seed, with " stearine,"	0·924	8·60	8·60
,, without ,,	0·923	9·60- 9·30	9·45
Sesamé, Senegal, . . .	0·9215	8·95- 8·50	8·70
,, Indian, . . .	0·921	7·40	7·40
Arachis, African, . . .	0·916	6·70	6·70
,, white, . . .	0·916	6·50	6·50
Colza, French, . . .	0·9142	6·40 ?	6·40 ?
,, Indian, . . .	0·9137	5·90- 5·80 ?	5·85 ?
Olive, ...	0·9155	5·30 ?	5·30 ?

Although this method will give concordant results under constant conditions it cannot be regarded as giving absolute values, and a perfect method of determining the oxygen absorption has yet to be devised.

Several factors have to be taken into account. Thus, *Lippert* has shown (*vide supra*) that in damp weather the oxygen absorption of oils containing manganese driers has a tendency to be lower, although oils poorer in manganese take up more oxygen under such conditions than those rich in that substance.

CHEMICAL CHANGES OCCURRING DURING DRYING OF OILS.

The nature of the chemical changes taking place during the complete atmospheric oxidation and consequent drying up of a drying oil has been the subject of various investigations; but it can hardly be said that the matter is yet settled beyond dispute.

The earlier researches on linseed and other drying oils by Mulder and others led to the conclusion that the chief constituent of drying oils, giving them their peculiar properties, was *linolin*, the glyceride of *linolic acid*, regarded as $C_{16}H_{28}O_2$, and then termed *linoleic acid*. During drying this glyceride was supposed to become hydrolysed or otherwise broken up, losing its glyceridic character, and forming *hydroxylinoleic acid*, $C_{16}H_{26}O_5 . 2H_2O$, by oxidation; a neutral polymerised amorphous anhydro derivative, *linoxyn*, $C_{32}H_{54}O_{11}$, being subsequently developed as the chief ingredient of the " skin " formed as the oil dries.

Livache[1] has shown that so-called non-drying oils, such as rape and olive oils, also yield an elastic product (Mulder's linoxyn) when kept at a higher temperature (120° to 160° C.), and that even solid animal fats show the same phenomenon. Hence he regards the distinction between drying and non-drying oils as only permissible when understood as referring to ordinary temperatures.

Later researches have indicated that what was formerly termed "linoleic acid," $C_{16}H_{28}O_2$, is probably a mixture of three acids of notably higher molecular weights—viz., *true linolic acid*, $C_{18}H_{32}O_2$, related to oleic acid as oleic acid is to stearic; and two isomeric acids still less saturated, related to linolic acid in the same way, *linolenic* and *isolinolenic acids*, both represented by $C_{18}H_{30}O_2$. These substances by gentle oxidation yield crystallisable acid products, *sativic acid* (tetrahydroxystearic acid), melting at 173° C., being formed from linolic acid, and *linusic* and *isolinusic acids* (hexahydroxystearic acids), melting at 203° to 205° C. and 173° to 175° C. respectively (*vide* p. 51), being produced from the other two acids. But these crystallisable ultimate oxidation products are apparently not formed in the "boiling" process at all; and even if contained in the dried skins are certainly not the constituents giving the peculiar physical properties to these substances. Moreover, the proportions of oxygen and water which must be taken up by linolic and linolenic glycerides in order to convert them into free hydroxystearic acids, are greatly in excess of the increment in weight observed to take place during the drying of oils of this class (*vide supra*); whilst the skins are found to be susceptible of some degree of saponification, furnishing glycerol. Hence it would seem probable that the essential constituents of dried skins are a mixture of polymerised glycerides (possibly more or less hydrolysed) of acids derived from linolic, linolenic, and isolinolenic acids by oxidation processes not carried so far as to produce the various hydroxystearic acids obtainable by means of alkaline permanganate.[2] That some of these substances are of a feebly acid character, or at any rate are capable of forming salts by the action of metallic oxides, is suggested by the well-known fact that the effect of basic matters like white lead (basic lead carbonate) and zinc white (chiefly zinc oxide) on the paint produced by their admixture with drying oils is different in many respects from that of neutral pigments like lead sulphate and sulphate of barium. In practice these latter are found to be far less suitable for the production of firm adherent coats that will stand ordinary wear and tear, which is usually considered to be due to the absence of the metallic salts contained in white lead and zinc white paints, formed by the neutralisation of acids developed by oxidation, or possibly by the saponification of glycerides

The drying qualities of an oil appear to be the more marked the greater the proportion of linolenic and isolinolenic acids present.

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[1] *Comptes Rendus*, 1895, cxx., 842.

[2] *Cf.* Fahrion's experiments *infra*.

Hazura and *Grüssner* calculated the following percentages from the relative proportions in which the hydroxystearic acids were produced on oxidising the liquid fatty acids of linseed, hemp-seed, nut, poppy-seed, and cotton-seed oils, the solid acids being previously separated by conversion into lead salts and treatment with ether.

	Linolenic Acid.	Isolinolenic Acid.	Linolic Acid.	Oleic Acid.
Linseed oil, ...	15	65	15	5
Hemp-seed oil, . . .	15		70	15
Nut oil, ...	13		80	7
Poppy-seed oil, . . .	5		65	30
Cotton-seed oil, . . .	...		60	40

Bauer and *Hazura* considered the drying of oils as being mainly due to the linolenic and isolinolenic acids, which, by taking up oxygen, become converted into the "oxylinoleic acid" of Mulder, which they regarded as $C_{18}H_{30}O_7$. For the most part, however, the glyceridic character of the product is not destroyed during the oxidation, so that, instead of free acid, a neutral body results, substantially the "linoxyn" of Mulder, but termed by them *hydroxylinolein*. Small quantities of free fatty acids are, however, developed by the decomposition of the glycerides of the solid fatty acids present (myricin, palmitin, etc.); the glycerol of these glycerides being converted into carbon dioxide and other volatile products.

According to experiments by *Cloez*,[1] the effect produced by prolonged exposure to air of a drying oil is not quite so simple as would appear from the above. The following figures were obtained with linseed and poppy-seed oils, the final increase in weight being a little more than 7 per cent. in each case after eighteen months:—

Linseed Oil.

	Before Exposure.	After Oxidation.	
		Percentage Composition.	Calculated per 100 Parts of Linseed Oil originally used.
Carbon, . . .	77·57	67·55	72·30
Hydrogen, . . .	11·33	9·88	10·57
Oxygen, . . .	11·10	22·57	24·16
	100·00	100·00	107·03

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[1] *Bull. Soc. Chim.*, 1865, iii., 49.

Poppy-seed Oil.

	Before Exposure.	After Oxidation.	
		Percentage Composition.	Calculated per 100 Parts of Linseed Oil originally used.
Carbon, . . .	77·50	66·68	71·38
Hydrogen, . .	11·40	9·94	10·64
Oxygen, . . .	11·10	23·38	25·03
	100·00	100·0	107·05

The original oils thus had a composition closely akin to that of a triglyceride of an acid of formula $C_{18}H_{32}O_2$, requiring carbon 77·90, hydrogen 11·16, oxygen 10·94 per cent. During oxidation, from $\frac{1}{12}$ to $\frac{1}{14}$ of the carbon disappeared and not far from the same proportion of hydrogen. Even if the whole of the glyceridic part of the oil had been oxidised to volatile products, only $\frac{1}{19}$ of the carbon would have disappeared; so that, obviously, carbon dioxide, or acetic acid, etc., must have been formed at the expense of the fatty acids present, indicating a more deep-seated oxidation change than the simple absorption of oxygen, with the conversion of the glycerides of linolenic and isolinolenic acids into hydroxylinolein.

In the case of castor oil, *Cloez* found the gain in weight after eighteen months to be much less marked (2·68 per cent.), whilst only a practically inappreciable amount (0·4 per cent.) of the original carbon had disappeared. Intermediate results were obtained with a semi-drying oil, sesamé oil, the gain in weight in eighteen months being 4·83 per cent., and the loss of carbon about $\frac{1}{17}$ of the original amount.

Fahrion[1] found that the fatty acids obtained on saponifying boiled linseed oil were not completely soluble in petroleum spirit, whereas the fatty acids of unoxidised oil readily dissolved in that solvent. From 0·6 to 31·6 per cent. of such insoluble acids were found in different specimens of oil. The proportion present appears to be the greater the more marked the decrease in the iodine absorption caused by the oxidation process. These oxy-acids readily dissolve both in alcohol and in ether (*cf.* Chap. VI.).

The same observer, in later work on the same subject,[2] came to the conclusion that, in the atmospheric oxidation of linolic acid (from cotton-seed oil), a series of oxidised acids was formed, in which 1, 2, 3, and 4 atoms of oxygen were successively added, the final product being a tetroxylinolic acid.

In the case of linolenic and isolinolenic acid, he concluded that a similar series of acids was produced, the final one being an anhydride of hexoxylinolenic acid, $C_{18}H_{28}O_7$ ($= C_{18}H_{30}O_8 - H_2O$). Similarly, jecoric

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[1] *Zeit. angew. Chem.*, 1891, 540; 1892, 171.

[2] *Chem. Zeit.*, 1894, xvii., 1848.

acid was said to yield, as its final product, a double anhydride of pentoxyjecoric acid, $C_{18}H_{26}O_5$ ($= C_{18}H_{30}O_7 - 2H_2O$).

As the oxidation proceeds the fatty acids become more solid, and the solubility in ether decreases, whilst the solubility of the barium salts in water increases. The " oxidised acids " are soluble in dilute ammonium hydroxide, and *Fahrion* effected a partial separation of the different acids by fractionally precipitating them from such solution by means of barium chloride.

Autoxidation Theory.—*Fokin*, in a series of experimental researches,[1] concluded that the drying of linseed oil was due to a hemi-molecular autoxycatalysis, which was promoted by the peroxides of certain metals such as lead, cobalt, manganese, etc.

Fahrion,[2] however, considered that the experimental evidence did not support this view. By successively extracting oxidised fatty acids of linseed oil with cold petroleum spirit, ether, and alcohol, he separated the autoxidation products of linolic and linolenic acids.

The elementary composition of these acids was in favour of the conclusion that they were mixtures of diperhydroxylinolenic acid, $C_{18}H_{30}O_6$, and perhydroxylinolic acid, $C_{18}H_{32}O_4$. The former was regarded as a derivative of the latter, which had all the characteristics of *Mulder's* " white linoxy-acid," which undergoes a molecular transformation into *Mulder's* " red linoxy-acid."

This change is probably due to the formation of an inner ester, analogous to the change undergone by ricinoleic acid.

From further experiments, in which siccatives were added to linseed oil fatty acids, the conclusion was drawn that the chemical process of drying is not altered by such addition, but that the autoxidation is accelerated. In its essential details the autoxidation of linseed oil follows the same course as that of the free fatty acids.

Later researches into the nature of the changes which take place in the drying process indicate that at certain stages, at all events, there is a polymerisation of the molecule.

Morrell[3] concludes from his experiments that thickening by polymerisation occurs when there are at least two pairs of doubly-linked carbon atoms in the molecules of the fatty acids, and that, prior to polymerisation, there is a shifting of the linkages in the molecule. In the first stage of the thickening due to polymerisation products insoluble in acetone are formed, whilst at higher temperatures the final stage is the formation of polymerisation products insoluble in petroleum spirit.

Morrell's[4] further experiments on the properties of cerium salts obtained from drying oils also support his view that there is a change in the intramolecular linkings prior to polymerisation when drying oils are polymerised by heat.

In the case of the cerium salt, α-elæostearate prepared from tung

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[1] *Zeit. angew. Chem.*, 1909, xxii., 1451, 1492.

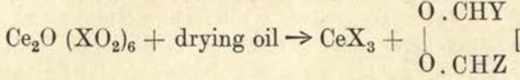
[2] *Ibid.*, 1910, xxiii., 722.

[3] *J. Soc. Chem. Ind.*, 1915, xxxiv., 105.

[4] *J. Chem. Soc.*, 1918, cxiii., 111.

oil, he represents its function in the drying process by the following scheme :—

$$CeX_3 \text{ or } CeOX_6 \rightarrow Ce_2O\,(XO_2)_6$$



$$Ce_2O\,(XO_2)_6 + \text{drying oil} \rightarrow CeX_3 + \begin{array}{l} O.CHY \\ | \\ O.CHZ \end{array} \text{[oxidised oil]},$$

where CeX_3 represents a salt of the normal type, and $CeOX_6$ and $Ce_2O(XO_2)_6$ are basic salts formed from the normal salt by the absorption of oxygen. This representation agrees with the conclusions of *Ingle*[1] concerning lead linolenate.

Acrolein has been detected in the gaseous products formed when linseed oil or its fatty acids are oxidised, under pressure, at 100° C. with oxygen. *Salway*[2] explains this oxidation on the assumption that linolenic acid contains the grouping—

$$R\,.\,CH:CH\,.\,CH:CH\,.\,CH\,.\,CH:CHR'.$$

The acid is first oxidised, with the formation of an oxygenide, which tends to form a dioxygenide, and the latter would then decompose with the production of a mixture of aldehydes, including acrolein, and of carbon monoxide and dioxide.

In the drying of linseed oil it is probable that the glyceride is first oxidised in stages as above, and that the mixture of aldehydes polymerises and combines with the unchanged part of the oil to form the elastic varnish.

Various conditions affecting the oxidation of linseed oil have been studied by *Holden* and *Radcliffe*.[3] They have found that the velocity of drying increases with the temperature, but that the higher the temperature the lower is the maximum increase in weight, and the less the accelerating influence of any drier. When dried at a temperature just below 34° C., linseed oil gains 17 to 18 per cent. in weight, but at 100° C. the maximum increase is much less (*e.g.*, 7 to 8 per cent.) ; whilst at 150° C. there is no increase in weight, which is probably due to the evolution of volatile products.

Equal drying capacity is shown by the linoleate or resinate of the same metal, but manganese has six times the efficiency of lead. The greater durability of linseed oil films dried at high temperatures is attributed by *Holden* and *Radcliffe* to the more rapid volatilisation of the non-drying constituents. These affect the hardness of the oxidation product. They find that the volatile products of linseed oil oxidised in air at 100° C. contain unsaturated aldehydes and drops of an oily substance, and in this respect their results confirm those of *Salway* (*supra*). The drying of linseed oil is accelerated by ultra-violet rays. These decompose the non-drying constituents, as is shown by the fact that linseed oil oxidised under their influence only gains 12 to 13 per cent. in weight.

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[1] *J. Soc. Chem. Ind.*, 1917, xxxvi., 319.

[2] *J. Chem. Soc.*, 1916, cix., 138.

[3] *J. Soc. Dyers and Col.*, 1918, xxxiv., 138.

POUTET'S ELAIDIN REACTION—NITROUS ACID TEST.

Oils containing olein and its homologues, or ricinolein, undergo a marked change when treated with nitrous acid, becoming more or less solidified without alteration of composition, whereas linolin, linolenin, and isolinolenin remain fluid under the influence of the reagent. Gaseous nitrous anhydride (fumes from nitric acid heated with starch or arsenious anhydride) will produce the reaction, or agitation with substance containing nitrous acid dissolved—*e.g.*, red nitric acid, solution of a nitrite recently acidified, copper or mercury recently dissolved in nitric acid, or even nitric acid warmed until it begins to act on the oil.

Poutet's Reagent.—The liquid originally described by *Poutet* in 1819 is obtained by dissolving 12 parts by weight of mercury in 15 of cold nitric acid (sp. gr. 1·35).[1] In making the test, 2 c.c. of the fresh solution and 50 of oil are shaken together in a bottle at intervals for about two hours, at the end of which time the action is nearly complete, although the product usually becomes stiffer or harder on standing twenty-four hours. Olive oil of good quality thus treated gives a bright yellow extremely hard "elaidin;" arachis and lard oils yield products little inferior in stiffness; mustard, rape, sesamé, sunflower, cotton-seed, and other oils give softer products, varying in consistency from a stiff buttery mass to a mixture of pasty product with still fluid substances; whilst linseed and other drying oils are comparatively little affected.

Classification of Oils according to the Elaidin Test.—*Allen* classifies the more important fixed oils as follows, in accordance with the physical character of the product:—

Solid Hard Mass.	Buttery Mass.	Pasty or Buttery Mass separating from a Fluid Portion.	Liquid Products.
Olive oil.	Bottlenose oil.	Rape oil.	Linseed oil.
Almond oil.	Mustard oil.	Mustard oil.	Hemp-seed oil.
Arachis oil.	Neat's foot oil	Sesamé oil.	Walnut oil.
Lard oil	Arachis oil } Sometimes.	Cotton-seed oil.	
Sperm oil.	Sperm oil	Sunflower-seed oil.	
Neat's foot oil (sometimes).	Rape oil	Niger-seed oil.	
		Cod-liver oil.	
		Whale oil.	
		Porpoise oil.	

In certain cases (more especially with olive oil) the nature and consistence of the elaidin formed on treatment with nitrous acid affords a useful means of detecting the presence of adulterations with oils of different character. In all such cases, the most satisfactory

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[1] Archbutt (*J. Soc. Chem. Ind.*, 1886, v., 303) dissolves 18 grammes of mercury in 15·6 c.c. of nitric acid, sp. gr. 1·42 (22·2 grammes of acid), and uses 1 part of the resulting green fluid to 12 of oil (by weight).

results are obtained when the oil examined is tested side by side in the same way with samples of oil of standard purity, and of the same mixed with known proportions of other oils.[1]

Fatty Acids.—The free fatty acids obtained by saponifying oils and decomposing the resulting soaps with a mineral acid are affected by nitrous acid in similar fashion. Attempts have been made to utilise, for candle-making and other purposes, the polymerised solid acids of higher melting point thus formed; but, hitherto, various practical difficulties have stood in the way of utilising the products effectively.

Legler's Consistence Tester.—*Legler* has constructed a simple form of apparatus by means of which comparative tests can be made of the degree of consistence of the elaidin mass produced when any given oil sample is treated with nitrous acid. It consists of a piece of glass tubing narrowed at one end (Fig. 37). Through the tube passes a glass rod supported by means of a spiral spring, and furnished with a horizontal disc on the top, so that by placing weights on the disc the end of the rod is depressed to an extent proportionate to the weight added. The outer tube is held vertically by a suitable clamp holder, so adjusted that the bluntly pointed end of the rod just rests on the surface of the elaidin to be tested. The measurement is made by placing a given weight on the disc and noting how far the rod sinks into the elaidin in a given time (*e.g.*, a minute), by reading off the level on a scale the zero point of which is level with the top of the outer tube when the disc is unweighted. The elaidin samples are best prepared by mixing together 10 c.c. of oil, 10 c.c. of nitric acid of 25 per cent., and 1 gramme of copper wire or turnings, and allowing to stand twenty-four hours; the mass is fused by dipping the containing vessel in warm water so as to bring about complete separation of elaidin and watery fluid, and the former removed and allowed to solidify. To obtain comparable results, a uniform method of manipulating should be adopted, the samples tested being examined side by side with others similarly prepared from genuine oils or known mixtures.

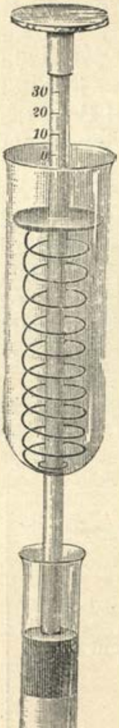

Fig 37.
Legler's
Consistence
Tester.

Exposure of olive oil to sunlight greatly diminishes the solidity of the elaidin formed from it; the nature of the change brought about is uncertain; probably oxidation takes place with formation of hydroxyolein, as the exposed oil develops more heat by the action of sulphuric acid than the original oil kept in darkness (*vide* p. 216).

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[1] There is often great difficulty experienced in obtaining absolutely pure samples of oil for use as standards. In many cases it is only possible to obtain such standard substances by actual expression of hand-picked seeds, etc., in the laboratory, and subsequently refining the product; but this is not readily practicable, unless a plentiful supply of pure seed is to hand, as well as a good form of small experimental or laboratory press.

Farnsteiner[1] made various attempts to effect a quantitative conversion of oleic acid into elaidic acid, but without success. The best yields were obtained by means of an apparatus, in which the oleic acid was placed in a small flask, the air partially removed, and a given quantity of nitric oxide introduced, followed by sufficient oxygen to combine with it. The most favourable conditions for the absorption were when the temperature was maintained at 10° to 20° C., and when the ratio of oleic acid to nitric oxide was 1 gramme to 20 to 25 c.c. of gas. The solidification then occurred very rapidly, and a hard crystalline acid was obtained, which melted at about 43° C., and contained at least 82 to 96 per cent. of pure elaidic acid. *Farnsteiner* regards this method of applying the reaction used in conjunction with a treatment of the lead salts with ether (*infra*) as a valuable qualitative test for the presence of oleic acid in a mixture of fatty acids.

Lead elaidate resembles the lead salts of saturated fatty acids as regards its solubility in ether and benzene. According to *Farnsteiner's* experiments[1] its solubility at 16° to 20° C. is 0·0046 to 0·0086 in 100 c.c. of ether, and 0·004 gramme in 100 c.c. of benzene. This method would probably afford a means of separating oleic acid quantitatively from other liquid unsaturated fatty acids if it were possible to convert the whole of the oleic acid into elaidic acid.

By treating the liquid fatty acids of butter fat with nitrogen peroxide, and subsequently crystallising the lead salts of the product with ether, about 45 per cent. of lead elaidate was separated.

Action of Nitric Acid.—According to *Edmed*[2] when oleic acid is treated with nitric acid of specific gravity 1·2 to 1·3 formation of elaidic acid is the only reaction, and by using acid of density not exceeding 1·25 the yield of elaidic acid (m.p. 45° C.) is quantitative. The nitric acid must first be freed, by boiling from nitrous acid, which has a similar action.

Lewkowitsch[3] doubts the possibility of *Edmed* having really obtained so large a yield of pure elaidic acid.

Influence of Temperature.—*Lidow*[4] obtained a substance melting at 42° C. by the action of nitrous oxides on oleic acid at 0° C., whilst the increase in weight was 1 per cent. At 80° to 85° C. the weight was increased by 16·6 per cent. By continuing the action of the nitrous acids for a long period the elaidic acid first formed became liquid again.

As regards the temperature at which the test should be made, *Archbutt*[5] came to the conclusion that it should not be lower than 25° C., and should be uniform throughout. In his opinion the time required for solidification is of much more importance than the consistency of the product obtained.

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[1] *Zeit. Untersuch. Nahr. Genussm.*, 1899, ii., 1.

[2] *Proc. Chem. Soc.*, 1899, xv., 190.

[3] *Analyst*, 1900, xxv., 66.

[4] *Pharm. Zeit. Russland*, 1895, xxxiv., 105; *Analyst*, 1895, xx., 178.

[5] *J. Soc. Chem. Ind.*, 1886, v., 304.

Action of Nitric Acid on Fats.

When fixed oils are brought into contact with nitric acid a complex effect is often produced, oxidation of a part of the oil by the acid being brought about with the evolution of lower oxides of nitrogen, which convert the olein constituent of the oil into elaidin.

Bouveault[1] has found that a large number of dibasic acids are produced, including succinic, adipic, glutaric, pimelic, and sebacic acids, and describes a method of separating these from one another.

In some cases characteristic colours are produced with oils of pure nature. Thus when pure olive oil is treated with one-ninth its volume of nitric acid of specific gravity 1·42, the mixture being gently warmed in a large basin until the acid begins to act vigorously, and then stirred briskly (the source of heat being removed) until no further action is visible, a pale yellow solid mass is formed after standing an hour or two; whereas, if cotton-seed oil be present, a much darker tinted product is formed, which does not set so readily; and analogous results are obtained when various other oils are present.

The following colour tests, based on the action of nitric acids, have been proposed:—

(*a*) *Hauchcorne's Test*, as extended by *Stoddart*.—Agitate together from 3 to 5 measures of the oil with 1 of nitric acid of specific gravity 1·32. Heat the tube for five minutes in boiling water; then take it out and allow it to stand. Observe the colour of the oil from time to time for one and a-half hours.

(*b*) *Massie's Test*.—Agitate 3 measures of the oil for two minutes with 1 measure of colourless nitric acid of specific gravity 1·40. Observe the colour of the oil after separation.

(*c*) *Glassner's Test*.—Pour the oil cautiously into an equal measure of red fuming nitric acid, and observe the colour of the oil and of the zone which forms between the oil and the acid liquid.

As a rule, not much reliance can be placed on the results obtained by these tests, except in the case of cotton-seed oil (*q.v.*).

ZINC CHLORIDE REACTION.

Some oils, more especially castor oil, when heated in contact with a highly concentrated solution of zinc chloride, become converted into a gristly mass, which, on treatment with water to dissolve out the zinc chloride, breaks up more or less into fibrous portions, which swell up to a large extent to white masses closely resembling rasped cartilage, the oil being completely solidified by the process. Apparently, the chemical action consists chiefly of polymerisation, somewhat after the fashion of the elaidin reaction, possibly accompanied by dehydration. By long-continued boiling of the product with alkalis, partial saponification is effected, glycerol being set free.

To produce the most gristly product, the following process may be

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[1] *Bull. Soc. Chim.*, 1898, xix., 562.

followed[1]:—Zinc chloride solution is evaporated until the boiling temperature rises to about 175° C. or upwards, the composition of the fluid then being close to that indicated by the formula $ZnCl_2$, H_2O, or slightly less hydrated. Three parts of this fluid by weight, and one of castor oil, are then well intermixed together at a temperature of 125° C. or thereabouts. The oil speedily becomes more viscid, and then coagulates to a leathery mass resembling bullock's liver, but tougher, and separates for the most part from the zinc chloride in so doing. This mass is then chopped up, soaked in water till disintegrated to a mass somewhat resembling coarsely-scraped horse-radish, drained from zinc chloride solution and washed, when it is in suitable condition for use in the manufacture of india-rubber substitutes, insulating coatings for electric leads, etc.

By using weaker zinc chloride, or smaller proportions, or lower temperatures, the action can be controlled and stopped before going quite so far, so as to produce substances of less cartilaginous and more plastic character; or other oils, less readily acted upon, may be mixed with the castor oil; or resin, kauri gum, and similar substances may be added.

Colour Test.—When zinc chloride solution of somewhat lesser strength (of thick syrupy consistence when cold) is mixed with certain oils, colours are developed.

Thus, according to *Chateau*, 5 drops of syrupy zinc chloride stirred in a white crucible with 10 drops of the oil give practically no coloration with poppy, nut, almond (hot-pressed), gingelly, coconut, neat's foot, lard, horse, bone, whale (sometimes violet tinge), sperm, and cod-liver oils; whilst with certain other oils the colorations vary from yellowish-red or brown to green or blue. Little reliance can be placed on this test, which is due to the presence of impurities in the oils.

Action of Zinc Chloride on Oleic Acid.—Zinc chloride, when heated with oleic acid, converts it into a solid isomeride closely resembling elaidic acid. Thus, when oleic acid, mixed with 10 per cent. of its weight of zinc chloride, is heated to 180° to 185° C. (but not exceeding 195° C.) for some time, the transformation is so far complete that a sample taken out and treated with hot dilute hydrochloric acid yields a layer of fatty acids, solidifying on cooling. By diluting with water and subjecting the product to distillation with superheated steam (or under diminished pressure), a buttery mass is obtained which, on pressing (first cold and then hot), finally yields a hard crystallisable material of melting point 41° to 42° C., suitable for making certain kinds of candles not requiring fatty matter of high fusing point (Schmidt's process). *Benedikt* obtained the following results on analysis of the products thus formed:—[2]

A. Crude product obtained by boiling the heated mass with diluted hydrochloric acid.

B. Product of distillation under diminished pressure.

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[1] Eng. Pat. No. 9580, 1886, Muirhead and Alder Wright.

[2] *Monatsh. f. Chem.*, 1890, ii., 71; *J. Soc. Chem Ind.*, 1890, ix., 658.

C. Solid mass, after pressing until the melting point rises to 41° to 42° C.

	A.	B.	C.
Liquid anhydride.	8	..	..
Stearolactone,	28	31·0	75·8
Hydroxystearic acid,	17	..	..
Oleic and isoleic acids,	40	43·3	15·7[1]
Saturated fatty acids,	7	12·1	8·5
Unsaponifiable matters,	..	13·6	..
	100	100·0	100·0

The "unsaponifiable matters" contained in B were mainly liquid hydrocarbons of the olefine series (carbon = 84·1, hydrogen = 13·7, oxygen = 2·2).

It would appear that the general character of the main action is that zinc chloride combines directly with the oleic acid, and that the resulting compound (or, possibly, pair of isomeric compounds) is partly decomposed again into oleic and isoleic acids, and partly hydrolysed with formation of hydroxystearic acids, more especially the γ acid, which then loses the elements of water, forming stearolactone (*vide* p. 45); the hydrolytic action probably being as follows:—

$$\begin{array}{ccccccc} \text{Oleic Acid.} & & \text{Zinc Chloride.} & & \text{Compound of Zinc Chloride and Oleic Acid.} & & \\ C_{18}H_{34}O_2 & + & ZnCl_2 & = & C_{18}H_{34}O_2,ZnCl_2 & & \\ \text{Compound.} & & & & & & \text{Hydroxystearic Acid.} \\ C_{18}H_{34}O_2,ZnCl_2 & + & H_2O & = & ZnCl_2 & + & C_{18}H_{36}O_3 \end{array}$$

In all probability, similar reactions occur when glycerides containing olein are saponified by means of sulphuric acid, the yield of *liquid* oleic acid in the products finally obtained by distillation with superheated steam being very small.

ACTION OF SULPHURIC ACID ON OILS AND FATS. TURKEY RED OILS.

When sulphuric acid is added to a fixed oil or fat, various effects may be produced. In many instances distinctive colours are developed, due not so much to the action of the acid on the glycerides themselves as upon other bodies accompanying them in small proportion; this is especially marked in the case of certain fish liver oils where biliary constituents are present (*vide infra*). In other cases action occurs between the acid and the glyceride, producing more or less marked heat development, sometimes leading to charring and destruction, sometimes to less deep-seated changes of a definite character. Thus, when oils mainly consisting of olein are cautiously mixed with sulphuric

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[1] Isoleic acid only.

acid hydrolysis ensues, the resulting glycerol being more or less converted into *glycerosulphuric acid*, much as ordinary alcohol is into ethylsulphuric acid.

$$\begin{array}{ccccccc} \text{Alcohol.} & & \text{Sulphuric Acid.} & & \text{Ethylsulphuric Acid.} & & \text{Water.} \\ C_2H_5 . OH & + & SO_2\left\{\begin{matrix} OH \\ OH \end{matrix}\right. & = & SO_2\left\{\begin{matrix} O . C_2H_5 \\ OH \end{matrix}\right. & + & H_2O \\ \text{Glycerol.} & & \text{Sulphuric Acid.} & & \text{Glycerosulphuric Acid.} & & \text{Water.} \\ C_3H_5\left\{\begin{matrix} OH \\ OH \\ OH \end{matrix}\right. & + & SO_2\left\{\begin{matrix} OH \\ OH \end{matrix}\right. & = & SO_2\left\{\begin{matrix} O . C_3H_5(OH)_2 \\ OH \end{matrix}\right. & + & H_2O \end{array}$$

Action of Sulphuric Acid on Oleic Acid.—Simultaneously the oleic acid is acted upon, direct combination taking place between the two acids, with the formation of *hydroxystearosulphuric acid*, or *sulphostearic acid*.

$$\begin{array}{ccccccc} \text{Oleic Acid.} & & \text{Sulphuric Acid.} & & \text{Hydroxystearosulphuric Acid.} & & \text{Water.} \\ C_{17}H_{33} . COOH & + & SO_2\left\{\begin{matrix} OH \\ OH \end{matrix}\right. & = & SO_2\left\{\begin{matrix} O . C_{17}H_{34} . CO . OH \\ OH \end{matrix}\right. & + & H_2O \end{array}$$

This product, being a saturated compound, does not combine with iodine like the original oleic acid (*Benedikt* and *Ulzer*). Under the influence of hydrolysing agents it breaks up into hydroxystearic and sulphuric acids, thus[1]:—

$$\begin{array}{ccccccc} \text{Hydroxystearosulphuric Acid.} & & \text{Water.} & & \text{Sulphuric Acid.} & & \text{Hydroxystearic Acid.} \\ SO_2\left\{\begin{matrix} O . C_{17}H_{34} . CO . OH \\ OH \end{matrix}\right. & + & H_2O & = & SO_2\left\{\begin{matrix} OH \\ OH \end{matrix}\right. & + & C_{17}H_{34}\left\{\begin{matrix} CO . H \\ OH \end{matrix}\right. \end{array}$$

According to *Müller-Jacobs*, the product thus formed contains the elements of a molecule of water less $C_{18}H_{34}O_5S$ instead of $C_{18}H_{36}O_6S$: and is represented by him as a sort of sulphonic acid, $C_{17}H_{32}\left\{\begin{matrix} SO_2 . OH \\ CO . OH \end{matrix}\right.$, breaking up on hydrolysis with the formation of hydroxystearic acid, $C_{17}H_{34}\left\{\begin{matrix} OH \\ CO . OH \end{matrix}\right.$, hydroxyoleic acid, $C_{17}H_{22}\left\{\begin{matrix} OH \\ CO . OH \end{matrix}\right.$ being also formed, probably by a secondary action. *Geitel* considers that a mixed glyceride is formed, part of the three oleic radicles being modified by direct addition of sulphuric acid so as to form a glyceride in which the radicle of hydroxystearosulphuric acid partly replaces the oleic radicle, saponification of the glyceride not taking place, at any rate, at first.

Liechti and *Suida* also considers a mixed glyceride to be the first product containing simultaneously the radicles of sulphuric and hydroxystearic acids, thus—

$$\begin{array}{ccccccccc} \text{Triolein.} & & \text{Water.} & & \text{Sulphuric Acid.} & & \begin{matrix}\text{Hydroxystearosulphuric} \\ \text{Diglyceride.}\end{matrix} & & \text{Oleic Acid.} \\ 2C_2H_5\left\{\begin{matrix} O . C_{18}H_{33}O \\ O . C_{18}H_{33}O \\ O . C_{18}H_{33}O \end{matrix}\right. & + & 4H_2O & + & SO_2(OH)_2 & = & \begin{matrix} C_2H_2\left\{\begin{matrix} O . C_{18}H_{35}O_2 \\ OH \\ O \end{matrix}\right. \\ \left.\begin{matrix} \end{matrix}\right\} SO_2 \\ C_2H_2\left\{\begin{matrix} O \\ OH \\ O . C_{18}H_{35}O_2 \end{matrix}\right. \end{matrix} & + & 4C_{18}H_{35}O_2 \end{array}$$

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[1] The effect of sulphuric acid in decomposing fatty glycerides, together with the hydrolysing action of water on the product, has been utilised in the preparation of candle material. A larger yield of solid matter is thus obtained than by the ordinary saponification processes, on account of the conversion of liquid oleic acid into solid substances. According to *Geitel*, *γ-hydroxystearic acid* is usually produced (*inter alia*) by the hydrolysis of the compound of oleic acid with sulphuric acid, which immediately splits up into water and stearolactone (see Chap. XVI.).

Simultaneously (in their opinion) an analogous mixed diglyceride is formed, containing the radicle of hydroxyoleic acid ($C_{18}H_{33}O_2$) instead of that of hydroxystearic acid ($C_{18}H_{35}O_2$), this substance being produced in virtue of an oxidising action exerted by the sulphuric acid, whereby SO_2 is evolved.

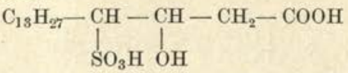
Inasmuch as practically no glycerol is obtainable from Turkey red oil by saponification (beyond what is due to the undecomposed original oil that is present), whilst free oleic acid gives products similar to those prepared from olive oil (the more free acid contained in the oil the better it is suited for the purpose), it is obvious that these mixed glycerides, even if formed under special conditions, are at any rate not the main constituents of the commercial products.

Lewkowitsch[1] considers the following course of reactions to take place :—

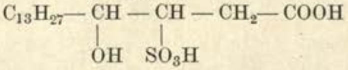
Assuming oleic acid to have the formula—

$$C_{13}H_{27}-CH=CH-CH-COOH,$$

it will combine with the sulphuric acid to produce the two sulphostearic acids in presumably equal proportions—

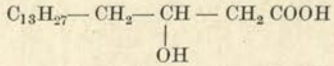
(1) 

$$C_{13}H_{27}-\underset{SO_3H}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_2-COOH$$

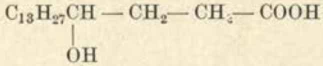
and (2) 

$$C_{13}H_{27}-\underset{OH}{\underset{|}{CH}}-\underset{SO_3H}{\underset{|}{CH}}-CH_2-COOH$$

Water is readily absorbed by these acids in sufficient quantity partially to convert them into sulphuric acid and β- and γ-hydroxystearic acids—



$$C_{13}H_{27}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2\,COOH$$

and 

$$C_{13}H_{27}\underset{OH}{\underset{|}{CH}}-CH_2-CH_2-COOH$$

the latter being immediately dehydrated with the formation of γ-stearolactone. Another portion of the sulpho-acids remains unchanged. On boiling the mass with water there is a further conversion of sulpho-stearic acids, but in order to obtain a suitable candle material it is necessary to distil the product, in which process the β-hydroxystearic acid is unfortunately converted into oleic and isooleic acids (see Chap. XVI.).

Action of Sulphuric Acid on Elaidic Acid.—*Tscherbakoff* and *Saytzeff*[2] have obtained a hydroxystearic acid ($C_{18}H_{36}O_3$) melting at 82° to 85° C., and conclude that this is identical with the hydroxystearic acid formed by the action of sulphuric acid on oleic acid.

"*Turkey Red*" *Oils.*—Products containing more or less hydroxystearosulphuric acid and the hydroxystearic acid thence formed by hydrolysis, together with unchanged olein, and some free oleic acid (also whatever solid fatty glycerides were originally present in the oil employed and the products of the action of sulphuric acid upon them) are manufactured from olive, cotton-seed, and similar oils chiefly consisting of olein, for use in dyeing and calico printing, especially in the production of "Turkey red," whence the name "Turkey red oils" applied to these products. The free acidity is usually partially or wholly neutralised by cautious addition of ammonia or other alkali to the oil after washing with brine or water.

[1] *J. Soc. Chem. Ind.*, 1897, xvi., 392.

[2] *J. prakt. Chem.*, 1898, lvii., 27.

According to *Juillard*[1] the following reactions take place on treating olive oil with sulphuric acid for the production of olive Turkey red oil:—The first action at 0° to 5° C. is described as the direct combination of one and of two molecules of sulphuric acid with olein forming mixed glycerides, containing simultaneously the radicles of oleic and oxystearosulphuric acids, and respectively indicated by the formulæ—

$$C_3H_5\left\{\begin{array}{l}O\,.\,CO\,.\,C_{17}H_{34}\,.\,O\,.\,SO_3H\\ O\,.\,CO\,.\,C_{17}H_{33}\\ O\,.\,CO\,.\,C_{17}H_{33}\end{array}\right.\quad\text{and}\quad C_3H_5\left\{\begin{array}{l}O\,.\,CO\,.\,C_{17}H_{34}\,.\,O\,.\,SO_3H\\ O\,.\,CO\,.\,C_{17}H_{34}\,.\,O\,.\,SO_3H\\ O\,.\,CO\,.\,C_{17}H_{33}\end{array}\right.$$

By the further action of sulphuric acid, these give rise to other more complex mixed glycerides containing simultaneously the radicles of sulphuric and oleic or oxystearosulphuric acids, and also that of a "polymerised" oleo-oxystearic acid, viz.:—

$$C_3H_5\left\{\begin{array}{l}O\,.\,CO\,.\,C_{17}H_{34}\,.\,O\,.\,CO\,.\,C_{17}H_{33}\\ O\,.\,CO\,.\,C_{17}H_{33}\\ O\,.\,SO_3H\end{array}\right.\quad\text{and}\quad C_3H_5\left\{\begin{array}{l}O\,.\,CO\,.\,C_{17}H_{34}\,.\,O\,.\,CO\,.\,C_{17}H_{33}\\ O\,.\,CO\,.\,C_{17}H_{34}\,.\,O\,.\,SO_3H\\ O\,.\,SO_3H\end{array}\right.$$

Commercial olive Turkey red oil chiefly consists of the sodium salts of these acids and of their derivatives and products of decomposition (oleic, oxystearic, oleo-stearic, oleo-oxystearic acids, etc.) formed during the process of washing out the uncombined sulphuric acid.

Action of Sulphuric Acid on Castor Oil.—Another variety of Turkey red oil, considerably superior for some special applications, is produced when castor oil is employed instead of olein-containing oils. According to the generally-received view, the chief action of the sulphuric acid is precisely analogous to that on ordinary alcohol. The glyceride is hydrolysed into glycerol and ricinoleic acid, the former being more or less converted into glycerosulphuric acid, as above; whilst the ricinoleic acid reacts on the sulphuric acid in a parallel way, forming *ricinoleosulphuric acid,* thus—

$$\underset{\text{Ricinoleic Acid.}}{C_{17}H_{32}\left\{\begin{array}{l}OH\\ CO\,.\,OH\end{array}\right.} + \underset{\text{Sulphuric Acid.}}{SO_2\left\{\begin{array}{l}OH\\ OH\end{array}\right.} = \underset{\text{Water.}}{H_2O} + \underset{\text{Ricinoleosulphuric Acid.}}{C_{17}H_{32}\left\{\begin{array}{l}O\,.\,SO_2\,.\,OH\\ CO\,.\,OH\end{array}\right.}$$

the resulting product differing from that formed from oleic acid in that it contains H_2 less, and is, therefore, an "unsaturated" compound, capable of taking up iodine or bromine in the same manner as the original ricinoleic acid itself (*Benedikt* and *Ulzer*). Accordingly, castor Turkey red oil is capable of taking up oxygen, and generally of behaving in ways not observed in the case of olive Turkey red oil; which circumstance renders it more suitable for certain particular applications in reference to dyestuffs, etc.

A somewhat different view of the action of sulphuric acid on castor oil was advanced by *Scheurer Kestner*[2] as the result of his investigations. After the glyceride had been hydrolysed, he found that part of the resulting ricinoleic acid became "polymerised" (or more accurately, dehydrated and "condensed"), so as to form a more complex molecule of *diricinoleic acid,* which was then acted upon by sulphuric acid

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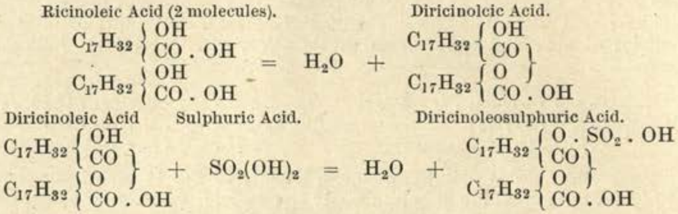
[1] *J. Soc. Chem. Ind.*, 1893, xii., 528.

[2] *Comptes Rendus*, cxii., 158 and 395; also *J. Soc. Chem. Ind.*, 1891, x., 471.

so as to form *diricinoleosulphuric acid*, as shown in the following equations :—



Ricinoleic Acid (2 molecules). Diricinoleic Acid.

$$\begin{matrix} C_{17}H_{32}\left\{\begin{matrix} OH \\ CO\,.\,OH \end{matrix}\right. \\ C_{17}H_{32}\left\{\begin{matrix} OH \\ CO\,.\,OH \end{matrix}\right. \end{matrix} = H_2O + \begin{matrix} C_{17}H_{32}\left\{\begin{matrix} OH \\ CO \end{matrix}\right. \\ C_{17}H_{32}\left\{\begin{matrix} O \\ CO\,.\,OH \end{matrix}\right. \end{matrix}$$

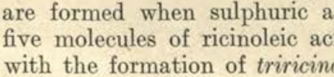
Diricinoleic Acid Sulphuric Acid. Diricinoleosulphuric Acid.

$$\begin{matrix} C_{17}H_{32}\left\{\begin{matrix} OH \\ CO \end{matrix}\right. \\ C_{17}H_{32}\left\{\begin{matrix} O \\ CO\,.\,OH \end{matrix}\right. \end{matrix} + SO_2(OH)_2 = H_2O + \begin{matrix} C_{17}H_{32}\left\{\begin{matrix} O\,.\,SO_2\,.\,OH \\ CO \end{matrix}\right. \\ C_{17}H_{32}\left\{\begin{matrix} O \\ CO\,.\,OH \end{matrix}\right. \end{matrix}$$

Obviously the diricinoleosulphuric acid thus formed is "unsaturated," and is, therefore, capable of taking up two halogen atoms for each C_{18} present. More or less of the diricinoleic acid escapes conversion into diricinoleosulphuric acid ; so that in addition to unaltered castor oil, etc., the resulting Turkey red oil consists of a mixture of diricinoleic acid and diricinoleosulphuric acid, together with some amount of ricinoleic acid that has escaped condensation to diricinoleic acid, and of ricinoleosulphuric acid formed by the direct action of sulphuric acid upon it. The non-sulphonated fatty acids tend to the development of blue shades with alizarin, whilst the ricinoleosulphuric acids tend to produce yellow shades.

Diricinoleosulphuric acid is hydrolysed by caustic alkali, the sodium or potassium salts or diricinoleic and sulphuric acids being formed if the action take place at temperatures below 80° C. ; but by prolonged boiling with alkali, or treatment therewith under pressure, water is taken up and ordinary ricinoleic acid regenerated by reversal of the two reactions above indicated. In just the same way ricinoleosulphuric acid becomes hydrolysed into sulphuric and ricinoleic acids, the action taking place extremely readily in presence of hydrochloric acid. In presence of sulphuric acid, Turkey red oil is apt to be yet further decomposed on heating, œnanthic acid, *inter alia*, being formed ; hence, in the preparation of the oil care must be taken that over-heating does not take place ; and similarly in washing out the excess of sulphuric acid, etc., with brine (to avoid solution of the soluble compound sulphuric acids formed), otherwise hydrochloric acid is apt to be formed and considerable loss of soluble acids occasioned by hydrolysis. Sodium sulphate is accordingly preferable to sodium chloride as diminishing this tendency to loss.

According to *Juillard*[1] acids still more highly "polymerised" than diricinoleic acid are formed when sulphuric acid acts on castor oil, three, four, and five molecules of ricinoleic acid becoming condensed and dehydrated, with the formation of *triricinoleic*, *tetraricinoleic*, and *pentaricinoleic* acids respectively. He regards the first action as giving rise, by partial hydrolysis and esterifying action jointly, to the product,



$$C_3H_5\left\{\begin{matrix} O\,.\,CO\,.\,C_{17}H_{32}\,.\,O\,.\,SO_3H \\ OH \\ O\,.\,CO\,.\,C_{17}H_{32}\,.\,OH \end{matrix}\right.$$

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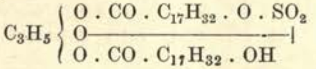
[1] *Bull. Soc. Chim.*, 1891, vi., 638 ; *J. Soc. Chem. Ind.*, 1892, xi., 355.

which then loses a molecule of water forming an anhydride, termed by him *diricinolein sulphuric anhydride*.



$$C_3H_5\left\{\begin{array}{l} O\ .\ CO\ .\ C_{17}H_{32}\ .\ O\ .\ SO_2 \\ O\text{————————————}| \\ O\ .\ CO\ .\ C_{17}H_{32}\ .\ OH \end{array}\right.$$

This reacts slowly with ricinoleic acid and sulphuric acid forming the various polyricinoleic acids above mentioned, and the polyricinoleo-sulphuric acids thence derived; so that commercial castor Turkey red oils are highly complex mixtures.

"**Sulpho-Fatty Aromatic Compounds.**"—*Twitchell*[1] has prepared a number of compounds in which an aromatic hydrocarbon is introduced as well as the sulphuric acid.

Thus benzene-stearo-sulphonic acid is obtained in accordance with the equation—

$$C_6H_6 + C_{18}H_{34}O_2 + H_2SO_4 = C_6H_4(SO_3H)C_{18}H_{35}O_2 + H_2O.$$

It is a sticky semi-solid mass which becomes viscous at 100° C. It differs from stearo-sulphuric acid in not being decomposed on boiling with water, and in yielding potassium sulphite instead of potassium sulphate on fusion with potassium hydroxide.

Naphthalene-stearo-sulphonic acid ($C_{10}H_6(SO_3H)C_{18}H_{35}O_2$) is a somewhat less fluid compound.

Phenol-stearo-sulphonic acid ($C_6H_3OH(SO_3H)C_{18}H_{35}O_2$) resembles the other compounds in character.

Products of this kind are used as catalytic agents in Twitchell's process of "fat-splitting" (*q.v.*).

Colour Reactions Produced by Sulphuric Acid.—In certain cases distinctive colorations are produced on mixing a drop of sulphuric acid with about 20 drops of oil, but as these are often due to impurities little reliance is usually placed upon such a test. It is of value, however, in the examination of marine animal oils. Thus, whale oil, when dissolved in carbon bisulphide (1 drop in 20) and treated with one drop of sulphuric acid, gives a fine violet coloration, quickly changing to brown. In the absence of the solvent, which probably modifies the violence of the reaction, only a reddish-brown colour, changing to black, is produced. This reaction is due to the presence of cholesterol and lipochromes in these oils (*cf. Cod-liver Oil*).

MAUMENÉ'S SULPHURIC ACID THERMAL TEST.

A considerable development of heat usually attends the chemical action brought about on mixing together a fixed oil and strong sulphuric acid; by making comparative observations in precisely the same way with standard pure oils, or known mixtures, and the substance to be tested, useful information can often be obtained as to the character, and to some extent the amount, of foreign admixture present.

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[1] *J. Amer. Chem. Soc.*, 1900, xxii., 22.

The results thus obtained, however, vary greatly with the conditions, because the rate of action, and consequently the rise in temperature, largely depends on the apparatus, on the way in which the intermixture is effected, and especially on the strength of the acid used.

The Maumené Test.—The details of the method as first used by *Maumené*, the originator of the process, are as follows :—

Fig. 38 represents a form of apparatus for applying the test ; a graduated cylinder, B, is provided with an india-rubber stopper, through which passes the stem of a thermometer, A, so graduated that the divisions are all above the stopper ; a short piece of quill tubing, C, also passes through the stopper, serving as a vent. 25 c.c. of oil are run into the cylinder, and then 5 c.c. of sulphuric acid, the latter by means of a pipette applied to the side of the cylinder, so that the acid falls to the bottom without mixing with the oil. The stopper and thermometer being inserted and the temperature taken, the end of C is closed by the finger, and the whole shaken up for a few seconds ; C is immediately unclosed, and the thermometer watched, so as to note the highest point to which it rises, and hence the range through which the chemical action has heated the mass.

In order to diminish errors due to radiation and convection, a small beaker may be used, jacketed outside with a somewhat larger one, the interspace being filled with cotton wool or fibrous asbestos. 50 grammes of oil and 10 c.c. of sulphuric acid are convenient quantities, the two being at the same temperature to start with ; the acid is run in slowly from a pipette, the mixture being vigorously stirred with a thermometer, and about a minute being allowed for the addition ; the temperature gradually rises to a maximum as the stirring is continued, remains nearly constant for a short time, and then falls again, the precise amount of rise depending, to some extent, on the way in which the admixture is made.

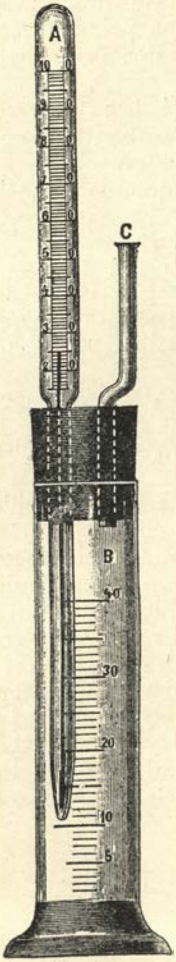

Fig. 38.
Apparatus for Maumené's Test.

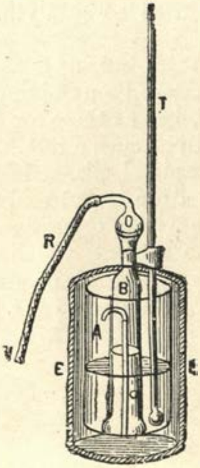

Fig. 39.
Jean's Thermelæometer.

A still more effective calorimeter is a vacuum-jacketed tube.

Jean's "Thermelæometer."—This is the name given by Jean[1] to his special form of apparatus shown in Fig. 39.

A is a small vessel 40 mm. diameter and 60 high, enclosed in a felt-lined case, E; this holds the oil (15 c.c.). B is a tube holding 5 c.c. of sulphuric acid (at 65° B.) furnished with a hollow glass stopper, to which is attached a piece of rubber tubing, R V; by blowing through the tubing the acid is forced out of the reservoir, B, and runs down on to the oil through the turned-over narrow exit pipe. T is a thermometer clamped to B. To use the instrument, the acid is introduced into B after removing the stopper, and the oil into A up to a given mark representing 15 c.c.; the oil is heated up to 40° to 50° C., the acid-holder placed in it, and the whole allowed to cool with occasional stirring to 30°; A is then placed in the casing, E, and the acid blown over into the oil, B, the attached thermometer being used as a stirrer, and a note taken of the highest temperature attained.

Comparative Results.—The following table exhibits some of Maumené's results, together with those subsequently obtained by others; numerous other analogous values have been recorded, exhibiting more or less marked differences according to the particular mode of manipulation adopted:—

	Maumené.	Allen.	Baynes.	Archbutt.
	Degrees.	Degrees.	Degrees.	Degrees.
Menhaden oil, ...	...	126	...	123 to 128
Cod-liver oil, . . .	102 to 103	113	116	...
Linseed oil, . . .	103	104 to 111	104 to 124	...
Walnut oil, . . .	101	...	...	...
Hemp-seed oil,. . .	98	...	...	...
Seal oil, ...	...	92	...	...
Whale oil, northern, .	...	91	...	...
,, southern, .	...	...	...	92
Poppy-seed oil. . .	74	...	...	86 to 88
Cotton-seed oil, crude, .	...	67 to 69	...	70
,, ,, refined, .	...	74 to 75	77	75 to 76
Arachis oil, . . .	67	...	...	47 to 60
Beech-nut oil, . . .	65	...	...	..
Rape and colza oils,. .	57 to 58	51 to 60	60 to 92	55 to 64
Almond oil, . . .	52 to 54	...	35	...
Horse foot oil, . . .	51	...	...	...
Tallow oil, . . .	41 to 44	...	...	...
Lard oil, ...	...	41	...	...
Sperm oil, . . .	...	45 to 47	...	51
Bottlenose oil, . . .	...	41 to 47	...	42
Olive oil, ...	42	41 to 43	40	41 to 45
Castor oil, . . .	47	65	...	46
Neat's foot oil, . .	...	...	...	43
Oleic acid, . . .	...	38·5	...	37·5

Obviously, an admixture of rape oil with linseed oil, or *vice versâ*, may be characterised with some degree of precision (the former yielding a value of little more than half that given by the latter), when the suspected sample is examined *side by side with samples of known purity*

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[1] *J. Pharm. Chim.*, 1889, xx., 339.

mixed in known proportions (*e.g.*, 2 to 1, equal proportions, or 1 to 2, and so on). Similarly with olive oil admixed with earth-nut oil, or with cotton-seed oil; or sperm oil mixed with fish oil.

Influence of the Strength of the Acid.—Commercial oil of vitriol varies considerably in its strength, sometimes containing 96 to 97 per cent. of true sulphuric acid, H_2SO_4, sometimes only 90 to 91 per cent., or even less. If the liquid be boiled in a retort under ordinary atmospheric pressure until about a quarter has distilled over, the residue when cool enough may be bottled and kept for use, being acid of about 98 per cent. strength.[1]

Archbutt[2] shows that the figures obtained by the older methods are liable to obscure variations. As regards the influence of the strength of the acid, he gives the following figures, *inter alia* :—

Real H_2SO_4 in the Acid.	Olive Oil.	Rise of Temperature.	
		Rape Oil.	Impure Olive Oil.
Per cent.		°C.	° C.
97·38	43·25	63 ; 62	48·5 ; 48·5
96·71	42	61	47 ; 47·5
94·72	36·5	54	40·75 ; 40·25
91·85	28 ; 29·25	40·5 ; 43	32·5 ; 32·5

He found that the rise of temperature was slow where acid of 94·72 per cent. strength was used, and very slow with 93·72 per cent. acid. He considered that there was no advantage in using acid of low strength, and therefore constantly employed that of 97 per cent.

This variation receives further illustration from the results of Thomson and Ballantyne and of Mitchell (*vide infra*).

Richmond[3] gives the following formula for correcting the results obtained with different strengths of acids to the standard of 100 per cent. H_2SO_4.

$$\text{Rise of temperature} \times \frac{21{\cdot}5}{\text{per cent. } H_2SO_4 - 78{\cdot}5} = \text{rise with 100 per cent. } H_2SO_4.$$

Specific Temperature Reaction.—In order to render the thermal test practically independent of variations in the strength of the sulphuric acid used, *Thomson* and *Ballantyne*[4] make simultaneously a comparative valuation with water, and calculate the ratio between

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[1] Pure "monohydrated" sulphuric acid, H_2SO_2, cannot be obtained by evaporation; when a strength of 98 to 98·5 per cent. is attained, the temperature rises to a point where the substance dissociates into water and sulphur trioxide, the latter passing off at the same rate as the water vapour, so that acid of that strength distils unchanged. Pure H_2SO_4 may be obtained by adding the calculated amount of SO_3 to oil of vitriol, strengthened by evaporation as far as possible; or by chilling the acid, and draining off the unfrozen mother liquor from the crystals of H_2SO_4 that form. When heated, SO_3 is evolved, and acid of about 98 per cent. left, which then distils unchanged.

[2] *J. Soc. Chem. Ind.*, 1886, v., 394.

[3] *Dairy Chemistry*, p. 278.

[4] *J. Soc. Chem. Ind.*, 1891, x., 233.

the heat developed with the oil examined and that with the water; the resulting ratio they term the *specific temperature reaction.* Thus the following figures were obtained with acid of different strengths, showing a considerably closer concordance between the "specific temperature reactions" than between the uncorrected values first obtained with the different strengths of acids; of course, *exact* agreement is not to be expected, as the heat development in the case of an oil is not brought about solely by the mere physical admixture, but is also influenced by the chemical changes set up, which necessarily are apt to vary with the strength of the acid :—

Substance used.	Sulphuric Acid of 95·4 per cent. H_2SO_4.		Sulphuric Acid of 96·8 per cent. H_2SO_4.		Sulphuric Acid of 99 per cent. H_2SO_4.	
	Rise in Temperature.	Specific Temperature Reaction.	Rise in Temperature.	Specific Temperature Reaction.	Rise in Temperature.	Specific Temperature Reaction.
	°C.		°C.		°C.	
Water, .	38·6	100	41·4	100	46·5	100
Olive oil, .	36·5	95	39·4	95	44·8	96
	34·0	88	38·1	92	44·2	95
	...	...	39·0	94	43·8	94
Rape oil, .	49·0	127	...	...	58·0	124
Castor oil,	34·0	88	37·0	89	...	...
Linseed oil,	104·5	270	...	...	125·2	269

In their method 50 grammes of water are mixed with 10 c.c. of sulphuric acid, each having a temperature of 20° C. The acid is introduced so as to occupy a minute in delivery. An error of 1 gramme too little in the weight of water raises the temperature by 0·8° C. A parallel determination is then made with the oil under examination. The figures thus obtained varied widely with different specimens of the same kind of oil, as is seen in the following table of results :—

Nature of Oil.	Specific Temperature Reaction. Water = 100.
Olive oil (13 kinds examined), ...	89 to 95
Cotton-seed oil (crude), ...	163
,, (refined—2 kinds), . . .	169 to 170
Rape oil (5 kinds), ...	125 to 144
Arachis oil (commercial), ...	137
,, (refined), ...	105
Linseed oil (4 kinds), ...	270 to 349
Castor oil (2 kinds), ...	89 to 92
Southern sperm oil, ...	100
Arctic sperm oil (bottlenose), . . .	93
Whale oil (pale), ...	157
Seal oil (4 kinds), ...	212 to 225
Cod oil (3 kinds), ...	243 to 272
Menhaden oil, ...	306

Relative Molecular Maumené Figures.—*Richmond*[1] believes that more than twice the amount of heat is evolved by glycerides of fatty acids with four unsaturated bonds than by those with two—*i.e.*, by linolic acid than by oleic acid. He attributes the heat to, firstly, hydrolysis of the glyceride, and, secondly, to the action on the unsaturated bonds. He calculates his results in connection with the percentage of potassium hydroxide consumed by the fat by means of the formula,

$$\text{R. M. M.} = \text{R} \times \frac{21{\cdot}5}{x - 78{\cdot}5} \times \frac{20 + h}{20} \times \frac{19{\cdot}5}{k},$$

where R represents the observed rise in temperature, x the percentage of H_2SO_4 in the acid, h the absorption capacity (for heat) of the apparatus, and k the percentage of KOH absorbed by the fat.

Hehner and *Mitchell*[2] do not agree with Richmond's conclusion as to the different relative proportions of heat evolved by oleic and linolic acid, and their view is supported by Mitchell's later experiments (*infra*).

Influence of Too High a Temperature.—When sulphuric acid is mixed with highly unsaturated oils, such as linseed or marine animal oils, the action is very violent, and there is an evolution of gas which leads to the loss of heat.

This fact was recognised by *Maumené*,[3] who recommended dilution with olive oil, so that the temperature should not rise so high as to char the mixture. He also recommended that trials should be made with different proportions of oil and acid, *e.g.*—

50 grammes oil to 18 c.c. acid.
50 „ „ 36 „
100 „ „ 18 „

Ballantyne and *Thomson* made use of this addition in determining their figures for cod, seal, linseed, and menhaden oils given in their table (*supra*). They used 20 grammes of the oil with 30 grammes of olive oil.

Addition of Mineral Oil.—*J. C. Ellis*[4] found that when the temperature exceeded 60° C. it was impossible to obtain concordant results. He therefore advocated diluting the oil with a mineral oil of specific gravity 0·915.

As the rise of temperature with the mineral oil alone was very slow he mixed it with colza oil of known thermal value, and calculated the amount due to each gramme of the mineral oil.

Fifteen grammes of oil were placed in a beaker of about 50 c.c. capacity, and 5 c.c. of sulphuric acid (sp. gr. 1·84) allowed to run down the side so as to form a layer below the oil. The temperature was then taken, and the mixture stirred until the highest temperature was reached (one to two minutes). To avoid a temperature of 60° C. being reached he made experiments with different mixtures of the vegetable oil and mineral oil in the proportions of $\frac{1}{3}$, $\frac{1}{2}$, $\frac{2}{3}$, and $\frac{3}{4}$.

In this way the following results were obtained:—

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[1] *Analyst*, 1895, xx., 58.
[2] *Analyst*, 1895, xx., 146.
[3] *Comptes Rendus*, xxxv.; *J. Soc. Chem. Ind.*, 1886, v., 361.
[4] *J. Soc. Chem. Ind.*, 1886, 150, 361.

	Linseed (raw).	Linseed (boiled).	Poppy.	Nut.	Cod-liver.	Skate-liver.	Ling-liver.	Haddock-liver.
Rise for each gramme of oil, ...	7·62	6·63	4·62	4·80	7·42	7·94	5·88	7·35
Bromine absorption (*Mills* and *Akitt*), .	81·25	81·50	56·54	72·74	81·61	109·20	82·44	109·84

A similar addition of mineral oil was advocated by *Bishop.*[1] He mixed 10 grammes of the oil with 10 grammes of mineral oil, and added 20 grammes of sulphuric acid. From the rise in temperature of the mixture the rise obtained with 10 grammes of mineral oil alone was deducted, and the result multiplied by 2.

Bishop thus obtained the following results :—

	Calculated Rise in Temperature.
	° C.
I. Cod-liver oil (white), ...	100
II. ,, ,, (pale), ...	102
III. ,, ,, (brown), ...	102·5
IV. Earth-nut oil, ...	66
V. Mixture of II. (80) and IV. (20), . .	97
VI. Mineral oil, ...	14

The objections to this addition are that both olive oil and mineral oil vary in their behaviour with sulphuric acid, and there can thus be no certainty of different observers obtaining the same results.

Ratio between the Maumené Figure and Iodine Absorption.—*Hehner* and *Mitchell*[2] pointed out that even with these rough methods of determining the Maumené figure there was a certain proportion between the rise of temperature with sulphuric acid and the percentage of iodine absorbed. Thus, *Tennille*[3] gives the Hübl and Maumené figures for nine samples of lard, and the ratio between the two = 1·748. Similarly in the case of olive oil, for which the corresponding figures are given by *Lengfield* and *Paparelli*,[4] the Maumené figure multiplied by 2·1837 gives approximately the Hübl value.

But any given factor obtained by the older methods is not generally applicable, as is evident from the figures given by *De Negri* and *Fabris.*[5]

The mean ratio between the Maumené and Hübl figures of olive oil was found to be as 1 : 2·314. But applying this to the other oils

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[1] *J. Pharm. Chim.*, xx., 302.

[2] *Analyst*, 1895, xx., 146.

[3] *J. Amer. Chem. Soc.*, 1895, 33-41 ; *Analyst*, 1895, xx., 63.

[4] *Rev. Intern. des Falsifications*, 1892, v., 98.

[5] *Zeit. anal. Chem.*, 1894, 547.

analysed by the same chemists the results were widely divergent. Thus—

Oils.	Maumené Figure.	Hübl Value.	Calculated Iodine Value.
Olive (203 samples), . .	35	81	81
Earth-nut, ...	49	95 - 95·4	113 4
Hazel-nut, ...	35-36	86·2- 86·8	81- 83
Almond, ...	51-52	93 - 95·4	118-120
Rape, ...	92-95	108 -108·8	213-220
Hemp-seed, ...	95-96	157·5	220-222
Maize, ...	86	111·2-112·6	199
Cotton-seed, ...	50-53	106·9-110	115·7-122·6
Linseed, ...	122-126	158·7-159·78	282 -291·5

Nor does the method of dilution with mineral oil lead to any better agreement, for if we refer to the results of Ellis (*supra*) and compare the Maumené figures with the approximate mean iodine absorptions, taking the ratio between the figures of poppy oil as the standard—*i.e.*, $\frac{135}{4\cdot62} = 29\cdot2$ as the factor—we obtain the following figures, which obviously do not correspond :—

	Linseed (raw).	Linseed (boiled).	Poppy.	Nut.	Cod-liver.	Skate-liver.	Ling-liver	Haddock-liver.
Approximate iodine value, . . .	172	...	135	145	142	167	...	154·2
Calculated iodine value (Maumené figure × 29·2), . . .	222·5	193·5	135	140·16	214·6	229·8	171·7	214·6

Influence of Oxidation.—According to *Archbutt*, olive oil exposed to sunlight for some time develops considerably more heat with sulphuric acid than the same oil kept in the dark; 52·5° rise of temperature being noted by him instead of 41·5°.

A yet greater difference was observed by Ballantyne in the case of olive oil exposed to light for six months, and agitated daily so as to promote aerial oxidation (67° instead of 44°), analogous differences being also observed with several other kinds of oils similarly treated (p. 182).

To eliminate this source of error *Jean* (*loc. cit.*) recommends washing the oil with alcohol, or, still better, to apply the test to the fatty acids.

In this way he obtained the following results with his "thermeæometer" :—

Oil.	Rise of Temperature.	
	Neutral Oil.	Fatty Acids.
	° C.	° C.
Olive, ...	41·5	45
Linseed, . . .	61	109
Colza (French), . .	37	44
,, (Indian), . .	37	46

Mitchell's Modification.—The writer devised a modification[1] in which the great sources of error in the older methods are eliminated or reduced. It is based upon the dilution of all oils alike with carbon tetrachloride and the determination of the thermal rise with sulphuric acid as in the bromine thermal test (*q.v.*).

Two grammes of the oil are weighed into a vacuum jacketed tube, 10 c.c. of carbon tetrachloride added, the temperature of the solution taken, and 2 c.c. of sulphuric acid introduced.

Fatty Acids.

Oil.	Rise with H_2SO_4 (93·8 per cent.).	Calculated Iodine Value Rise × 7.	Bromine Thermal Rise.	Calculated Iodine Value Rise × 6.
	Degrees C.		Degrees C.	
1. Oleic acid I. (old), . .	11·8; 11·7	82·3	14·0	84·0
2. ,, II. ,, . .	11·3; 11·4	79·8	14·3; 14·2	85·8
3. Almond, . . .	13·6; 13·8	96·6	16·1	96·6
4. Earth-nut, . . .	12·5	87·5	14·2	85·2
5. Olive, ...	11·6	81·2	14·1	84·6
6. Cotton, ...	16·8	117·6	18·1	108·6
7. Maize I. (6 years old, rancid), .	18·4	128·8	18·4	110·4
8. ,, II., . . .	16·9	118·3	19·8	118·8
9. ,, III. (1898), . .	17·2	120·4	20·0	120·0
10. Sesamé, ...	16·0	112·0	18·1	108·6
11. Rape I., . . .	13·7	95·9	16·5	99·0
12. Poppy (1895), . .	17·8	124·6	20·4	122·4
13. Linseed I. (4 years old),	24·8	173·6	28·2	169·2
14. ,, II. (Calcutta), .	24·7	173·9	29·4	176·4
15. ,, II. (after 3 weeks),	27·6	193·2	27·9	167·4
16. ,, III (oxidised), .	21·5	150·5	21·7	130·2
17. ,, IV. (boiled 10 hrs.),	23·9	167·3	28·3	169·8
18. Tung I., . . .	23·2	162·4	21·2	127·2
19 Castor, ...	16·8	117·6	14·5	87·0
20. Cod-liver (old), . .	20·5	143·5	23·4	140·4
21. Whale (old), . . .	14·0	98·0	15·3	91·8
22. Butter I., . . .	8·1	56·7	5·8	34·8
23. ,, II., . . .	9·4; 9·1	65·8	6·0	36·0
24. Mutton-fat, . . .	9·6	67·2	8·6	51·6
25. Lard, ...	11·5	80·5	10·9; 10·8	65·4

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[1] *Analyst*, 1901, xxvi., *169*.

The liquid is continually stirred with a standard Jena thermometer graduated in tenths of a degree, and a note taken of the rise in temperature. Shortly before the end of the reaction the sulphonated product separates and rises to the surface of the carbon tetrachloride. In this way duplicate results can be obtained agreeing within 0·2 of a degree.

Fatty Acids.—The iodine value calculated from the Maumené figure as thus obtained is in direct proportion to the iodine value calculated from the bromine thermal value of the fatty acids of most unoxidised oils, as is seen in the preceding table.

Castor oil, tung oil, and apparently butter fat and animal fats rendered at a high temperature, form an exception to this rule. The effect of atmospheric oxidation in raising the Maumené figure is shown in Nos. 7 and 15.

In order that the results obtained by different chemists may be comparable, it is advisable that all the figures should be calculated on the basis of an apparatus with a bromine thermal factor of 5, and that the exact strength of sulphuric acid be given.

The Maumené test is now seldom applied, since as a sorting test it has been largely superseded by the bromine thermal value. *Marden* and *Dover*[1] have shown that the results obtained under standard conditions and expressed in calories per gramme of oil stand in close relationship to the iodine values of typical oils.

SULPHUR CHLORIDE REACTION.

Vulcanised Oils.—The use of sulphur chloride in "vulcanising india-rubber" is well known. A somewhat analogous change takes place when this substance (preferably diluted with light petroleum oil, carbon bisulphide, or other suitable solvent) is mixed with certain oils, more especially linseed oil. Solidification ensues, with the formation of a more or less leathery mass, which is employed to some considerable extent in the manufacture of insulating coverings for electric mains and leads, and similar purposes. During the action considerable quantities of hydrochloric acid are evolved, whilst the final product contains sulphur, some of which is in a condition insoluble in carbon bisulphide, apparently combined with the oil constituents. Hence the chemical action of sulphur chloride appears to be of a far more deep-seated nature than that of nitrous acid (elaidin reaction), where the solidification appears to be due simply to polymerisation or isomeric re-arrangement of atoms. Although no true oxidation takes place during the treatment, the term "oxidised oil" is often applied to this product in the trade, probably because the solidification brought about is somewhat akin in appearance to that effected when drying oils are oxidised by exposure to air, forming solid products.

Another kind of "vulcanised oil" is obtained by mixing flowers of sulphur with the oil to be treated, and then applying heat, much as in

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[1] *J. Ind. Eng. Chem.*, 1917, ix., 858.

the process of vulcanising india-rubber. In some cases the oils are previously partly saponified. By heating linseed oil to about 230° C., cooling it to 176° C. (350° F.), and then stirring in sulphur, an india-rubber-like mass is finally obtained, useful in the preparation of rubber substitutes. As in the treatment with sulphur chloride, hydrogen appears to be removed during the process, hydrogen sulphide freely escaping. This renders the manufacture an especially fœtid one unless great care be taken to destroy the evil-smelling vapours evolved, as, for example, by causing them to pass through a furnace before escaping into the factory chimney, or some analogous treatment.

Sulphur Chloride Test.—The effect of chloride of sulphur (diluted with carbon bisulphide) upon oils of various kinds is so far different that in certain cases it may be employed to discriminate one from another, or to test for admixture. As in all other analogous cases comparison of the sample tested with genuine oils, treated side by side, is necessary in order to obtain reliable results.

Bruce Warren[1] found that when 5 grammes of oil were mixed with 2 c.c. of carbon bisulphide and 2 c.c. of a mixture of equal volumes of carbon bisulphide and yellow sulphur chloride (free from dissolved sulphur) and the whole heated on a water-bath till action commenced, the products formed (after evaporating off carbon bisulphide) differed in weight and character according to the nature of the oil, being partly soluble in carbon bisulphide and partly insoluble. Thus poppy-seed and linseed oils gave the following figures (5 grammes used in each case):—

	Poppy-seed.	Linseed.	Mixture of Equal Quantities of the Two.
Soluble, . . .	1·96	0·78	1·10
Insoluble, . . .	4·50	5·58	5·37
Total, . .	6·46	6·36	6·47

Henriques[2] has shown that the drying properties of an oil do not stand in any relationship towards the amount of sulphur chloride which it must absorb to yield a solid product.

Lewkowitsch,[3] too, demonstrates the unreliability of some of Bruce Warren's experiments. The same chemist has also found that the action of sulphur chloride on the mixed fatty acids produces a semi-solid mass quite different from the solid substances formed from the glycerides.

The action of sulphur chloride on oils is to a large extent a process of addition on to the unsaturated molecules analogous to the absorption of halogen, though there is undoubtedly some degree of substitution, especially on raising the temperature of the mixture. It has, in fact,

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[1] *Chemical News*, 1888, lvii., 113.

[2] *J. Soc. Chem. Ind.*, 1894, xiii., 47.

[3] *Oils, Fats, and Waxes*, 228.

been shown by *Henriques* that the iodine values of oils are lowered by treatment with sulphur chloride.

Thermal Test.—*C. A. Fawsitt*[1] employs sulphur chloride, S_2Cl_2, purified by distillation, in the proportion of 2 c.c. to 30 grammes of oil, operating as in the case of Maumené's sulphuric acid test. Very considerable differences are observed with different oils as regards the amount of heat evolved, the rate of its evolution, and the formation or otherwise of hydrochloric acid gas. Thus the following figures were obtained, *inter alia* :—

Name of Oil.	4 c.c. Sulphur Chloride to 30 grms. Oil.			
	Gas Evolution.	Rise in Temperature.	Time in Rising.	Rise per Minute.
		Degrees C.	Minutes.	
Sperm, . .	Very small.	71	8	8·8
Seal, . .	None.	112	5	22·4
Whale, . .	Slight.	91	3	30·2
Neat's foot, .	,,	82	4	20·5
Rape, . .	None.	89	6	14·8
Cotton-seed, .	Slight.	93	6	15·4
Linseed, .	Considerable.	97	2	48·7
Olive, . .	Slight.	94	4	23·5
Cod-liver, .	Abundant.	103	3	34·3
Palm-nut, .	Slight.	9	7	1·4
Oleic acid, .	Considerable.	99	6	16·5
Stearic acid, .	None.	8	2	1·6

Name of Oil.	2 c.c. Sulphur Chloride to 30 grms. Oil.			
	Gas Evolution.	Rise in Temperature.	Time in Rising.	Rise per Minute.
		Degrees C.	Minutes.	
Sperm, . .	Very small.	37	16	2·3
Seal, . .	None.	45	10	4·4
Whale, . .	Slight.	57	6	9·4
Neat's foot, .	,,	51	7	7·3
Lard, . .	,,	40	16	2·4
Rape, . .	None.	23	10	5·3
Cotton-seed, .	Slight.	49	11	4·4
Linseed, .	Considerable.	57	5	11·4
Olive, . .	Slight.	52	6	8·7
Castor, . .	Abundant.	56	2	27·7
Cod-liver, .	,,	55	4	13·7
Palm, . .	,,	35	3	11·6
Palm-nut, .	Slight.	5	9	0·5
Rosin, . .	Abundant.	31	7	4·4
Oleic acid, .	Considerable.	53	6	10·6
Stearic acid, .	None.	5	7	0·7

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[1] *J. Soc. Chem. Ind.*, 1888, 552.

It would hence seem that the relative figures obtained with a given pair of oils often vary considerably according as 2 or 4 c.c. of sulphur chloride are used; so that the value of the test as applied to mixtures is somewhat doubtful.

If the reaction could be observed within a shorter space of time, it would probably be found that the rise in temperature would be proportional to the iodine value, or, in other words, the degree of unsaturation, as in the case of the bromine thermal value and, to a less extent, of the Maumené figure. But since the time occupied by the rise occupies in some cases over fifteen minutes, it is unlikely that concordant results would be obtained by different chemists with the same specimen of oil.

Action of Sulphur on Unsaturated Fatty Acids.

When oleic acid or oils containing unsaturated fatty acids are heated with sulphur, combination occurs with the formation of addition and, to a less extent, substitution compounds.

Altschul[1] concluded that at moderately low temperatures (130° to 150° C.) only addition compounds were produced.

Henriques,[2] however, contested this view, and asserted that even at such low temperatures there was some degree of substitution. He was able to prove that hydrogen sulphide was evolved on saponification, even when his process of cold saponification was used.

Miscellaneous Colour Reactions.

In addition to the colour reactions mentioned above, various others have been proposed. Of these the most satisfactory are *Becchi's test* for cotton-seed oil based upon the reduction of alcoholic silver nitrate, *Halphen's carbon bisulphide test* for cotton-seed oil, and the *Baudouin* or *Furfural test* for sesamé oil. These tests are described and discussed under cotton-seed oil and sesamé oil (*q.v.*).

Other reagents proposed are:—Stannic chloride, barium polysulphide, mercuric nitrate, *aqua regia*, gaseous chlorine, sodium hydroxide, and phosphoric acid. For the most part these give but little reliable information, except in certain special cases. Thus linseed oil, when saponified with sodium hydroxide, yields a light yellow soap solution, whilst, if fish oils are present, the solution is red or reddish-brown.

Phosphomolybdic Acid.—*Welmans*[3] proposed a colour reaction consisting in dissolving about 1 gramme of a fat or oil in 5 c.c. of chloroform, and shaking the mixture with 2 c.c. of a solution of phosphomolybdic acid or of sodium phosphomolybdate (freshly prepared) and a few drops of nitric acid. On standing, the upper layer was said to show a green coloration, changing to blue on the addition of alkali in the presence of cod-liver or vegetable oils, whereas animal oils were said to give no coloration.

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[1] *Zeit angew. Chem.*, 1895, 691.

[2] *J. Soc. Chem. Ind.*, 1899, xviii., 466.

[3] *Abst. J. Soc. Chem. Ind.*, 1892, xi., 548.

According to *Lewkowitsch*,[1] this can at best only rank as a preliminary test; for several kinds of vegetable oils were found by him to give less coloration than tallow oil, and, on the other hand, a slightly rancid lard gave almost the same amount of coloration as a vegetable oil. Moreover, pronounced colorations were produced by rosin and mineral oils.

DIFFERENTIATION OF OILS OF DIFFERENT CLASSES.

Distinction between Animal and Vegetable Oils.

Linolic Acid.—*Benedikt* and *Hazura*,[2] being unable to obtain sativic acid from animal fats, came to the conclusion that linolic acid was not a constituent of these, and that the oxidation test might, therefore, be employed to distinguish between animal and vegetable fats. The discovery of linolic acid in animal fats by Fahrion has been confirmed by Farnsteiner and others, and the method of Benedikt and Hazura is, therefore, untrustworthy.

Phytosterol Tests.—The fact that vegetable oils contain phytosterol, whilst animal oils and fats contain cholesterol, affords a much more reliable means of detecting animal fats in the presence of vegetable oils. The methods of applying these tests are described on p. 171, *et seq.*

Differentiation of Drying and Marine Animal Oils.

Apart from their drying properties, certain oils belonging to this class are distinguished by yielding insoluble compounds on treatment with bromine, and linseed oil yields so much more than other drying oils that the test can be made quantitative (see *Linseed Oil*). *Hehner* and *Mitchell*,[3] who devised this test, found that linseed oil yielded about 25 per cent. of an insoluble bromide, whilst walnut oil yielded from 1·5 to 2 per cent. Insoluble bromides in small proportion were also obtained with members of the rape oil class. Thus, rape oil itself gave 0·9 per cent., and mustard-seed oil 1·5 per cent.

Marine Animal Oils. — These oils were also characterised by yielding insoluble precipitates with bromine. Thus, cod-liver oil gave 43 per cent. of a solid substance mixed with a heavy insoluble oil, which decomposed on heating before its melting-point was reached. Similar compounds were obtained from cod oil (35·5 per cent.), shark oil (22 per cent.), and whale oil (25 per cent.). These bromides are evidently compounds of bromine with mixed glycerides containing linolenic or similar unsaturated fatty acids.

The proportion of linolenic hexabromide yielded by the free fatty acids also affords a means of distinguishing between certain oils. Thus *Hehner* and *Mitchell* (*loc. cit.*) found that linseed oil fatty acids yielded 18 to 20 per cent. of linolenic hexabromide, whilst walnut oil fatty acids gave about 1 per cent., and rape oil 3·6 per cent. of analogous compounds.

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[1] *J. Soc. Chem. Ind.*, 1894, xiii., 617.

[2] *Monatsh. f. Chem.*, 1889, 190.

[3] *Analyst*, 1898, xxiii., 315.

Marine animal oil fatty acids also gave white insoluble precipitates. Thus, in the case of cod-liver oil 18 per cent. of a white bromide was obtained. This turned brown when dried in the water-oven, and on further heating became metallic black and decomposed below 200° C. The air-dried substance contained 62·91 per cent. of bromine, the theoretical amount in linolenic hexabromide being 63·31 per cent.

Halphen[1] has described a modification of Hehner and Mitchells' method. His reagent consists of 28 parts by volume of glacial acetic acid with 4 parts of nitrobenzene and 1 part of bromine. About 0·5 gramme of the oil under examination is shaken with 10 c.c. of this reagent in a stoppered tube until the liquid is homogeneous, and then allowed to stand.

No turbidity is obtained with olive, almond, castor, cotton-seed, poppy, lard, or neat's foot oils, whilst Jaffa sesamé oil and certain specimens of the foot oil of the horse and sheep yield a slight turbidity.

A marked turbidity, and eventually a heavy precipitate, is obtained with the following oils:—Nut oil (after five minutes), hemp-seed, linseed, seal, cod-liver, whale, sperm, and Japanese fish oils.

Rape oil is distinguished by giving a turbidity, which separates on standing into two layers of liquid.

These insoluble precipitates vary in their behaviour towards carbon tetrachloride. After being washed with ether and pressed between filter paper, they are mixed with boiling carbon tetrachloride in the proportion of 2·5 c.c. to 0·1 gramme. The linseed oil precipitate yields a clear solution which, on cooling, gradually deposits a gelatinous precipitate. With fish oils, on the other hand, the solution is opalescent, and only deposits a trace of a crystalline precipitate on cooling.

The bromides of other drying oils resemble linseed in this respect, but in the case of hemp-seed oil several hours are required before the gelatinous precipitate is deposited.

The other marine animal oils mentioned above all yield opalescent solutions, whilst in the case of the foot oils a clear solution which does not yield any precipitate is obtained.

According to *Halphen* it is possible by this test to detect 10 per cent. of linseed, hemp-seed, whale, or fish oil in castor, cotton-seed, or olive oils.

A quantitative test for the presence of marine animal oils in vegetable oils has been based by *Eisenschiml* and *Coptherne*[2] on the fact that the bromides from the former are insoluble in chloroform, whilst the linseed oil bromide is soluble. Fish oils that have been heated to 260° C., however, cannot be detected in this way.

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[1] *J. Pharm. Chim.*, 1901, xiv., 359, 391.

[2] *J. Ind., Eng. Chem.*, 1910, ii., 28.

CHAPTER VIII.

QUANTITATIVE REACTIONS OF OILS, ETC.

SEVERAL quantitative chemical tests are used for the purpose of obtaining information on various points connected with the general chemistry of fatty matters, so as to afford evidence in cases of suspected adulteration, etc. Some of these depend on the occurrence of saponification changes; others on different principles. Among them may be reckoned the determination of the amount of unsaponifiable matter present effected, as described on p. 169, and the valuation of the amount of free fatty acids present, not contained as glycerides (*vide* p. 166). In addition to these, the following tests, named after the various chemists who have proposed them, are also more or less frequently employed :—

1. *The Saponification or Koettstorfer Value.*—Determination of the number of milligrammes of potassium hydroxide (KOH equivalent = 56·1) required to saponify 1 gramme of the substance.

2. *The Hehner Value.*—Determination of the percentage of fatty acids, insoluble in hot water, contained in the fat.

3. *The Reichert Value.*—Determination of the proportion of acids formed, volatile with the steam of water when distilled under certain arbitrary conditions.

4. *The Iodine (or Bromine) Value (Hübl's Test).*—Determination of the quantity of iodine (or bromine) capable of direct combination with 100 parts of substance.

5. *The Acetyl Value (Benedikt and Ulzer's Test).*—Determination of the amount of acetic acid formed on acetylating substances containing alcoholiform hydroxyl. The results are expressed in milligrammes of potassium hydroxide corresponding to the acetic acid formed, and calculated on 1 gramme of acetylated product.

I. THE SAPONIFICATION VALUE—KOETTSTORFER'S TEST.

Owing to the different molecular weights of the various fatty acids contained in glycerides and compound esters, it necessarily results that equal weights of different substances are chemically equivalent to different amounts of alkali—*i.e.*, that the quantities of potassium hydroxide, for example, required to bring about the saponification reaction

Glyceride. Potassium Hydroxide. Glycerol. Potassium Soap.

$$\left.\begin{matrix}C_3H_5\\X_3\end{matrix}\right\}O_3 \quad + \quad 3KOH \quad = \quad \left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3 \quad + \quad 3KOX$$

vary with the nature of X when equal weights of fatty matter are used throughout. The greater the molecular weight of X, the less potassium hydroxide will be required to saponify a given weight. The quantity of potassium hydroxide necessary for saponification, being a measure of the molecular weight of the fatty glycerides, etc., present, was shown by Koettstorfer to afford in many cases a useful means of checking the nature and purity of the oil, etc., examined. The weight of potassium hydroxide (KOH = 56·1) thus consumed by 1,000 parts of substance (milligrammes of potash per gramme) is accordingly known as the "Koettstorfer number" (*Verseifungszahl*); or otherwise as the "*Saponification Value*" or "*Total Acid Value*" of the oil, etc., examined. The determination of this value is effected in somewhat the same fashion as that of the "Acid Value" described in Chap. VI., by saponifying the oil with a measured excess [1] of alcoholic potassium hydroxide, and titrating the unneutralised surplus. In this way the potassium hydroxide consumed represents, not only the free fatty acid present, but also that liberated during saponification—*i.e.*, the *total* fatty acids present—whence the name.

The saponification value, K, of a given substance being known, the mean equivalent weight of the substance is readily calculated by the proportion

$$K : 56{\cdot}1 :: 1{,}000 : x = \frac{56{,}100}{K}.$$

The value of x thus obtained is generally referred to as the "*saponification equivalent*" of the body in question.

The following table represents the saponification values and saponification equivalents of various triglycerides and compound esters of frequent occurrence. In the case of glycerides the molecular weight is three times the saponification equivalent, whilst with compound esters of monohydric alcohols the two values are identical.

Saponification Values of Common Oils and Fats.—The table on p. 227 gives the values collected by *Schädler* [2] and by *Benedikt* [3] from various sources.

More recent values are given in the table on p. 228, which includes the results of several observers.

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[1] Unless a considerable excess be used, it is very difficult to ensure complete saponification.

[2] *Untersuchungen der Fette, Oele, und Wachsarten*, 217.

[3] *Analyse der Fette und Wachsarten*, 2nd ed., 294.

Substance.	Chief Sources.	Saponification Value, or Koettstorfer Number (Mgrms. of KOH required for Saponification, &c., of 1 grm.).	Saponification Equivalent.
Glycerides.			
Tributyrin, . .	Butter fat,	557·3	100·7
Trivalerin, . .	Porpoise, dolphin, and whale oils,	489·2	114·7
Trilaurin, . .	Coconut and palm-nut oils,	263·8	212·7
Tripalmitin, . .	Palm oil, lard,	208·8	268·7
Tristearin, . .	Tallow, lard, cacao butter,	189·1	296·7
Triolein, . .	Olive and almond oils,	190·4	294·7
Trierucin, . .	Colza and rape oils,	160·0	350·7
Trilinolin, . .	Linseed, hemp, maize, and walnut oils,	191·7	292·7
Triricinolein, .	Castor oil,	180·6	310·7
Compound Esters.			
Cetyl palmitate, .	Spermaceti,	116·9	480
Myricyl palmitate,	Beeswax,	83·0	676
Ceryl cerotate, .	Chinese wax,	71·2	788
Dodecatyl oleate, .	Sperm oil,	124·7	450
Dodecatyl doeglate,	Bottlenose oil,	120·9	464

Practical Determination of Saponification Values of Glycerides, etc.

(*a*) *Hot Saponification.*—A known weight of the substance to be examined (conveniently 2 or 3 grammes) is accurately weighed in a flask, and 25 c.c. (or other suitable quantity) of standard (approximately semi-normal) alcoholic potassium hydroxide added. This should be made from alcohol—not methylated spirit—that has been treated with potassium hydroxide, and distilled so as to remove as far as possible all compound esters and other impurities that might be resinised, or otherwise partially neutralise alkali. Methylic alcohol of high purity may be similarly used, preferably after the same treatment. The whole is heated on a water-bath under a reflux condenser,

Name of Oil, &c.	Schädler.	Benedikt
Apricot-kernel,	192-193	192·9
Arachis,	194-196	190·1-197
Almond, sweet,	190-192	187·9-196·1
,, bitter,	...	194·5-196·6
Butter,	225-230	227
Beeswax (yellow),	95-100	97-107
Bone oil,	190-191	...
Cacao butter,	198-200	...
Coconut,	255-260	255
Colza,	177-178	175-179
Curcas,	230-231	230·5
Charlock,	176-177	...
Castor,	201-203	176-181·5
Carnauba wax,	...	79
Cotton-seed,	194-195	191-210·5
Cod-liver, medicinal,	175-185	171-213·2
,, brown,	180-200	
Galam butter,	192-193	...
Gundschit (lallemantia),	184-185	185·0
Hemp-seed,	192-194	193·1
Hedge radish,	176-177	174·0
Japan wax,	222-223	...
Linseed oil,	190-192	187·4-195·2
Lard,	195-196	...
Malabar tallow (piney tallow),	191-192	...
Menhaden,	...	192
Maize,	188-189	188·1-189·2
Neat's foot,	191-193	...
Niger,	189-191	189-191
Nut (walnut),	196-197	196·0
Olive, salad,	191-193	185·2-196
,, inferior,	186-188	
,, -kernel,	188-189	188·5
Poppy,	193-194	192·8-194·6
Palm,	201-202	...
,, -kernel,	246-248	257·6
Pumpkin-seed,	189-190	189·5
Porpoise,	...	143·9 Fluid portion, 263·0
Pilchard,	...	186-187·5
Shark-liver,	...	84·5
Seal,	180-195	191-196
Sesamé,	192-193	187·6-192·2
Sunflower,	193-194	193
Spermaceti,	108	108·1
Sperm,	134	132·2
Suet (ox tallow, beef tallow),	193-195	...
Tallow (sheep),	192-195	...
Tacamahac,	199-200	...
Ungnadia,	190-192	...
Whale,	190-191	190-191
,, bottlenose,	...	197·3 Fluid portion, 290·0
Wool-grease,	169-170	...

Oil.	Saponification Value.	Authority.	Saponification Value.	Authority.
Apricot-kernel, .	188·0	Crossley and Le Sueur	192·2-192·9	De Negri and Fabris
Arachis, . .	185·6-194·8	Crossley and Le Sueur (Indian)	190·2-194	Sadtler
Almond, . .	189·5-191·7	De Negri and Fabris	187·9-192	Dieterich
Castor, . . .	176-178	Allen	176·7-179·1	Deering and Redwood (23 samples)
Cod-liver, . .	182-187	Allen	179-193·4	Parry and Sage
Colza, . . .	175-179	Allen	175-177	De Negri and Fabris
Cotton-seed, . .	191·6-193·5	Thomson and Ballantyne	191·8-193·8	De Negri and Fabris
Curcas, . . .	210·2	De Negri and Fabris	192·5-192·8	Archbutt
Hemp-seed, . .	190-191·1	Lewkowitsch	192-194·9	Shukoff
Japan wood (Tung),	155·6-172	De Negri and Fabris	190·7-196·1	Williams (12 samples)
Linseed,. . .	185-195	Allen	191·5	Crossley and Le Sueur
Maize, . . .	190·4	De Negri and Fabris	192·6	Winfield
Menhaden, . .	189	M'Ilhiney	192	Allen
Mustard-seed, .	171·2	Crossley and Le Sueur	173·9	Blasdale
Neat's foot, . .	194·3	Lewkowitsch	...	...
Niger-seed, . .	188·9-192·2	Crossley and Le Sueur	181·5-181·9	Mitchell
Olive, . . .	185-196	De Negri and Fabris (213 samples)	190·9	Crossley and Le Sueur (Indian)
Olive-kernel, . .	182·3-190·5	Klein	...	...
Poppy, . . .	193-195	De Negri and Fabris	189·0-196·8	Crossley and Le Sueur
Pumpkin-seed, .	192·5	Graham	189·3-189·9	Poda
Porpoise, . .	216-218·8	Allen	203·4	Bull
Seal, . . .	190·6	Bull	190·7-192·9	Fahrion
Sesamé, . . .	188-190	Shukoff	192-193	Thoerner
Shark, . . .	163·5	Bull	161	Lewkowitsch
Sunflower, . .	188-189	De Negri and Fabris	191·7-193	Shukoff
Whale, . . .	187·9-194·2	Schweitzer and Lungwitz	183·9-185	Bull

and gently agitated at intervals until complete solution has taken place. After a few minutes' more heating to ensure that saponification is complete, the unneutralised alkali is titrated with semi-normal standard acid (preferably hydrochloric), phenol-phthalein being used as indicator. The standardising of the alcoholic potassium hydroxide in terms of the acid is preferably effected by heating 25 c.c. on the water-bath under a reflux condenser *side by side with the oil examined*, and subsequently titrating the solution.

The difference between the amounts of acid required in the two cases thus directly corresponds to the amount of alkali required for the saponification, which is expressed in milligrammes for 1 gramme of fat. In the equation

$$K = \frac{n}{w} \times 56{,}100.$$

K represents the saponification value, n the number of c.c. of normal potassium hydroxide solution, w the weight of fat or oil taken, and 56·1 the molecular equivalent of potassium hydroxide (KOH).

Or the saponification equivalent may be calculated by means of the formula

$$E = \frac{w}{n}.$$[1]

(*b*) *Cold Saponification.*[2]—From 3 to 4 grammes of the fat are dissolved in 25 c.c. of petroleum spirit, and the solution mixed with 25 c.c. of standard alcoholic potassium hydroxide (containing as little water as possible). The saponification is usually complete in two or three hours, but it is advisable to leave the flask for twelve hours before titrating back the excess of alkali.

Eichorn[3] recommends the use of amylic alcohol in the place of ordinary alcohol in the determination of the acid and saponification values of waxes. In the case of the former value the advantage is that the titration can be completed without the necessity of reheating the solution, and any partial saponification is thus avoided. Hence the results are considerably lower than those obtained by the older method.

In determining the saponification value about 5 grammes of the wax are heated on the water-bath with 60 c.c. of amylic alcohol and 25 c.c. of N potassium hydroxide, a blank determination being made at the same time. The excess of alkali is titrated after thirty minutes, although experiments made by Eichorn show that saponification is complete in fifteen minutes.

The determination of the saponification value is generally combined with that of the acid value. The weighed quantity of fat, etc., mixed with a little warm alcohol, is titrated with alcoholic alkali, phenolphthalein being used as indicator, so as to determine the acid value. Excess of alkali is then added and the determination of the total acid number or saponification value proceeded with. Thus, suppose that 2·501 grammes (2,501 milligrammes) of Japan wax contain sufficient

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[1] 1 c.c. of "normal" acid represents E milligrammes of fat, whence n c.c. of acid are equivalent to $n \cdot E$ milligrammes. Since this quantity $= w$, it results that $E = \frac{w}{n}$. On the other hand, 1 c.c. of normal acid represents 56·1 milligrammes of KOH, whence n c.c. are equivalent to $n \times 56{\cdot}1$ milligrammes. Then $w : n \times 56{\cdot}1 :: 1{,}000 : K = \frac{n}{w} \times 56{,}100$.

[2] Henriques, *Zeit. angew. Chem.*, 1895, 721 ; 1896, 221.

[3] *Zeit. anal. Chem.*, 1900, xxxix., 640.

free fatty acid to neutralise 2·5 c.c. of semi-normal alkali (equal to 1·25 c.c. of normal solution); whilst, after adding excess of alkali, saponifying, and titrating back, 19·0 c.c. of semi-normal solution (equal to 9·5 c.c. normal) are neutralised in all; then the acid and saponification values are respectively $\frac{1·25}{2,501} \times 56,100 = 28·04$, and $\frac{9·5}{2,501} \times 56,100 = 213·1$; whilst the saponification equivalent is $\frac{9·5}{2,501} = 263·3$.

The Ester Value.—If A be the acid value, and K the saponification value (Koettstorfer number), the quantity K − A is a measure of the proportion of compound ethers (esters, glycerides, etc.) present in the substance examined, and may be conveniently termed the *ester value* (*Esterzahl*, *Ætherzahl*). Thus in the above instance the ester value is 263·3 − 28·04 = 235·26. In general, if m c.c. of normal alkali are consumed in neutralising the free acid present in w milligrammes of substance, and n c.c. in neutralising the total acids, the ester value, K − A, is given by the equation—

$$\mathrm{K} - \mathrm{A} = \frac{m}{w} \times 56,100 - \frac{n}{w} \times 56,100 = \frac{m - n}{w} \times 56,100.$$

In the case of triglycerides, the quantity of glycerol theoretically obtainable from a given weight of substance is readily calculated from the ester value: 3 × 56·1 parts of potassium hydroxide, neutralised by the acids liberated from the triglycerides, represent 92 parts of glycerol set free: hence, if S is the ester value, the glycerol produced is $\frac{92}{168·3} \times \mathrm{S} = 0·5466 \times \mathrm{S}$ per thousand, or $0·05466 \times \mathrm{S}$ per cent. Thus, a sample of arachis oil, showing the value 195·0, and the free acid value 5·0, and consequently the ester value 195·0 − 5·0 = 190·0, would theoretically yield 190·0 × 0·05466 = 10·39 per cent. of glycerol.

Proportion of Fatty Acids Liberated on Saponification.—Just as the average molecular weight of a mixture of triglycerides or other compound esters will depend partly on the molecular weights of the fatty acids liberated on saponification, and partly on those of the alcoholic or glyceridic constituents, so will the percentage of fatty acids obtainable vary in like manner. In the case of a mixture of glycerides in which some of the fatty acids are of low molecular weight obviously a smaller percentage of fatty acids will be formed than would be the case were all the fatty acids of higher molecular weight. Thus, 100 parts of butyrin, $C_3H_5(O \, . \, C_4H_7O)_3$, would theoretically yield 87·4 of butyric acid; whilst 100 parts of stearin, $C_3H_5(O \, . \, C_{18}H_{35}O)_3$, would similarly furnish 95·7 parts of stearic acid.

In certain cases, useful information may be obtained by determining the total percentage of fatty acids actually produced, more especially when, in addition to the total percentage, the amounts respectively *soluble* and *insoluble in water* are also found; the information being in some cases further supplemented by determining the amount and nature of alcoholic or glyceridic complementary products.

The total percentage of fatty acids may be reckoned from the amount of alkali required for saponification (the Koettstorfer number determined as indicated above), if the mean equivalent of the fatty acids is known. More usually, however, the latter is the principal point to be examined, and the percentage of acids requires to be directly determined; from which value, together with the quantity of alkali used, the mean equivalent weight of the fatty acids is calculated. Thus, if 100 parts by weight of substance yield a weight, w_1, of fatty acids (*i.e.*, if w_1 be the percentage of fatty acids found), and w_2 parts of potassium hydroxide, KOH, be required to neutralise these acids, the mean equivalent weight of the acids is given by the proportion—

$$w_2 : 56{\cdot}1 :: w_1 : x = \frac{w_1}{w_2} \times 56{\cdot}1.$$

If K be the total acid value (permillage of KOH, or ten times the percentage) the mean equivalent weight of the fatty acids will obviously be—

$$x = \frac{w_1}{\frac{1}{10}\,\mathrm{K}} \times 56{\cdot}1 = \frac{w_1}{\mathrm{K}} \times 561.$$

Neutralisation Value of the Fatty Acids (*Verseifungszahl der Fettsaüren*).—This term is conveniently employed to indicate the quantity of potassium hydroxide (KOH = 56·1) neutralised by 1,000 parts of the free acids. This value and the mean equivalent weight of the free acids are related to one another in a fashion similar to that exhibited by the total acid number (saponification value) and the saponification equivalent of the original fat or oil. If N be the neutralisation value of the free acids, and F their mean equivalent weight (value of x as above), then

$$\mathrm{N} : 56{\cdot}1 :: 1{,}000 : \mathrm{F},$$

whence

$$\mathrm{N} = \frac{56{,}100}{\mathrm{F}},$$

and

$$\mathrm{F} = \frac{56{,}100}{\mathrm{N}}.$$

The following table represents the average *neutralisation values of the free fatty acids* obtained from various kinds of oils, etc.—*i.e.*, the quantities of potassium hydroxide (KOH = 56·1) neutralised by 1,000 parts of mixed free fatty acids (*Schädler*):—

Name of Oil, &c.	Neutralisation Value.	Name of Oil, &c.	Neutralisation Value.
Almond, . . .	204-205	Olive, . . .	199-200
Arachis, . . .	196-197	Palm, . . .	206-207
Cotton-seed, . .	204-205	Palm-kernel, . .	265-266
Castor, . . .	187-188	Poppy, . . .	204-205
Cod-liver (medicinal),	202-204	Suet (ox), . .	205-206
Colza, . . .	181-182	Sesamé, . . .	197-198
Linseed, . . .	198-199	Sunflower, . .	201-202
Lard, . . .	215-217	Tallow (sheep), . .	206 207
Nut (walnut), . .	208-209		

In the case of a triglyceride, the calculated saponification equivalent of the glyceride always exceeds the equivalent weight of fatty acids produced from it by saponification by 12·67; for the general reaction of saponification being equivalent to

$$C_3H_5(OR)_3 + 3H_2O = C_3H_5(OH)_3 + 3HOR;$$

where R is a fatty acid radicle, it results that the molecular weight (three times the equivalent) of the glyceride, G, plus $3 \times 18 = 54$ parts of water, is identical with the molecular weight of glycerol = 92, plus three times the equivalent weight of the fatty acid formed by saponification, 3F; whence

$$G = 3F + 92 - 54,$$

and

$$\frac{G}{3} = F + 12{\cdot}67.$$

In similar fashion, in the case of a mixture of a triglyceride and the fatty acid which it contains (*e.g.*, tristearin and stearic acid), the mean saponification equivalent of the mixture will exceed the equivalent of the fatty acid by a fraction of the number 12·67, expressing the proportion of fatty acid contained as glyceride to the total fatty acid present. If S be the ester value and K the saponification value, this fraction is $\frac{S}{K}$; whence, the mean saponification equivalent of the mixture, M, is given by the equation

$$M = F + \frac{S}{K} \times 12{\cdot}67.$$

Thus, supposing the acid value to be 5 per cent. ($\frac{1}{20}$) of the saponification value, so that the ester value is 95 per cent. ($\frac{19}{20}$) thereof, the relationship between M and F will be

$$M = F + \frac{19}{20} \times 12{\cdot}67$$
$$= F + 12{\cdot}04.$$

Similarly, if the acid value be 10 per cent. ($\frac{1}{10}$) of the saponification value

$$M = F + 11{\cdot}40.$$

Hence, as in the case of most oils and fats, the amount of free acid is only a few per cents. of that of the total acids, it may be taken as a general rule that *the mean saponification equivalent of a natural oil or fat exceeds the mean equivalent of the fatty acids contained therein by about* 12; and by a proportionately less amount when the quantity of free fatty acid present increases beyond a few per cents.

This relationship enables comparisons to be readily instituted between the values obtained on the saponification of a fat or oil, and by titrating the separated fatty acids when expressed as equivalents; whereas, such comparisons are much less readily made by means of the milligrammes of potassium hydroxide per gramme of fat directly obtained, viz., the "total acid value" (saponification value) of the glyceride, and "neutralisation value" of the free acids thence derived.

Since the saponification equivalent of a triglyceride exceeds the equivalent weight of the fatty acid contained therein by 12·67, it results that for fatty glycerides, where the equivalent weight of the fatty acid contained lies between 250 and 330, the percentage of fatty acid yielded by the glyceride lies between $\frac{250}{250 + 12\cdot67} \times 100$, and $\frac{330}{330 + 12\cdot67} \times 100$—*i.e.*, between 95·2 and 96·3; so that for the great majority of natural oils and fats containing only small quantities of free fatty acids, the rest being glycerides, the yield of fatty acids per 100 parts of fat is close to 95·75 parts. Fats containing a considerable amount of glycerides of relatively low molecular weight, such as butter fat, coconut oil, and palm-kernel oil, etc., yield proportionately smaller percentages of fatty acids; on the other hand, if much free fatty acid be present in the fat or oil examined, the percentage yield of fatty acids from the mixture is proportionately increased.

Inner Saponification Value.—This is the term given by *Fahrion*[1] to the amount of potassium hydroxide required to neutralise the fatty acids in an oil or fat insoluble in petroleum spirit. The fatty acids from 2 to 3 grammes of the fat are liberated from the soap solution, the liquid extracted with petroleum spirit in a separating funnel, and the united extracts evaporated. The residue, consisting of unoxidised fatty acids and unsaponifiable matter, is dried to constant weight (1), and then dissolved in strong alcohol, and titrated with semi-normal alkali, the milligrammes of potassium hydroxide being calculated on 1 gramme of the original oil.

The neutral alcoholic solution is then extracted with petroleum spirit, the extract evaporated, and the residue of unsaponifiable matter dried and weighed (2).

The difference between (1) and (2) gives the amount of non-volatile fatty acids, whose molecular weight can be calculated from the inner saponification value. The oxidised fatty acids left in the separating funnel are dissolved out by means of hot alcohol, the solvent evaporated, and the residue dried to constant weight, ignited, the ash deducted, and the difference taken as oxidised fatty acids (3). The sum of (1) + (3) gives the Hehner value. The following results were obtained with cotton-seed oil and three oxidation products prepared by exposing the oil on wash leather for eight and twelve days respectively. The leather extracted with petroleum spirit gave products A and B, whilst B_1 was obtained by further extraction of the second leather with cold ether.

	Cotton-seed Oil.	A.	B.	B_1.
Iodine value, ...	108·8	55·4	46·3	29·1
Acid ,, ...	2·2	13·3	13·8	33·4
Saponification value, . . .	190·4	233·1	227·5	271·3
Inner saponification value, . .	186·9	128·8	128·9	74·4
Hehner value, ...	94·22	85·34	83·62	74·2
Unsaponifiable matter (per cent.),	1·10	1·11	1·28	0·72
Oxidised fatty acids, ,,	0·27	20·70	19·43	37·72
Non-volatile fatty acids, ,,	92·85	62·53	62·91	35·76
Molecular weight of fatty acids,	278·1	276·2	273·2	269·1
Melting point of fatty acids, .	35°-36° C.	45°-46° C.	46° C.	51° C.

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[1] *Zeit. angew. Chem.*, 1898, 781.

Fahrion considers that this method affords a means of examining the course of oxidation of linseed oil, and is also applicable to the examination of unoxidised fats and oils, as is shown in the examples.

	Ox Tallow.	Olive Oil.	Butter Fat.
Saponification value, . . .	193·9	188·4	225·9
Inner saponification value, . .	193·8	188·1	185·2
Hehner value, ...	95·58	95·25	87·60
Unsaponifiable matter, . . .	0·11	0·98	0·24
Oxidised fatty acids, . . .	0·13	0·18	0·14
Non-volatile fatty acids, . .	95·34	94·07	87·22
Molecular weight of fatty acids, .	275·0	280·1	263·7

These results show that when, as in the case of tallow and olive oil, the total saponification and inner saponification values are nearly identical, the amount of volatile or oxidised fatty acids must be very small, whereas butter fat, owing to its volatile acids, shows a considerable difference (40·7) between the two values.

II. THE HEHNER VALUE.

This test consists in determining that fraction of the fatty acids which remains insoluble in hot water, repeatedly applied until no more acid is dissolved. In the case of most oils and fats this quantity differs but little from the total percentage (about 95·5 to 96 per cent. as a rule, *supra*)—*i.e.*, only minute quantities of soluble fatty acids are present; but with cow's butter, coconut oil, and some few other substances, the difference is much greater. Thus, in the case of butter fat, the total percentage is usually from 93 to 94, whilst the percentage of insoluble acids (the Hehner number) is only 87 to 88. In the case of the fatty glycerides employed in the manufacture of oleomargarine, the soluble acids are present in only very small quantity, so that the insoluble acids amount to 95 to 96 per cent.; hence, any considerable admixture of oleomargarine with genuine butter is detected by the increase in percentage of insoluble acids found.

The table on opposite page represents the proportion of genuine butter fat and foreign fats (margarine) present in a sample of mixture yielding a higher Hehner value than genuine butter fat, *assuming this to give the value* 87·5, *and margarine to give* 95·5.

The same result can also be obtained by means of the formula

$$x = (H - 87{\cdot}5) \times 12{\cdot}5,$$

where H is the observed Hehner number, and x the calculated percentage of margarine.[1]

Other tests depending on principles somewhat similar to those involved in Hehner's test have been proposed by other chemists for use in special cases. Thus the difference in solubility of barium salts has been used as a criterion instead of the difference in solubility of free acids for butter analysis, etc.

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[1] When coconut oil (or the "stearine" separated from it by chilling and pressing) or palm-kernel oil is substituted for oleomargarine from beef suet, etc., this table does not hold good.

Hehner Value Found.	Percentage Present of	
	Genuine Butter Fat.	Margarine.
87·5	100	0
88	93·75	6·25
88·5	87·5	12·5
89	81·25	18·75
89·5	75	25
90	68·75	31·25
90·5	62·5	37·5
91	56·25	43·75
91·5	50	50
92	43·75	56·25
92·5	37·5	62·5
93	31·25	68·75
93·5	25	75
94	18·75	81·25
94·5	12·5	87·5
95	6·25	93·75
95·5	0	100

Practical Determination of the Amount of Fatty Acids formed on Saponification (Soluble and Insoluble in Water), and their Average Equivalent Weights.

Determination of Hehner Value.—The neutralised alcoholic solution left after determining the saponification equivalent (or the product obtained by saponifying a larger quantity of fat, say 10 grammes, with alkali without titration) is evaporated to drive off alcohol, dissolved in hot water, and treated with an excess of acid (standardised or otherwise, according to circumstances—*vide infra*); a few minutes' boiling decomposes all soap present, so that a clear layer of melted fatty acids rises to the surface on standing. A weighed filter (weighed in a dish after drying in the hot-water oven) is prepared and wetted with water (otherwise fatty acids may pass through), and the acidified fluid filtered, the oily fatty acids remaining on the filter being washed with boiling water until the filtrate is no longer acid. The filter is then dried inside the weighed dish, and thus the weight of insoluble acids determined. If w grammes of oil give n grammes of insoluble acids, the "Hehner value," H, or percentage of insoluble acids, is obviously

$$H = \frac{n}{w} \times 100.$$

Knight's Process.[1]—This is based on the insolubility of the barium salts of the higher fatty acids. From 1 to 3 grammes of the fat are saponified with alcoholic alkali, the alcohol evaporated, the soap solution diluted with cold water to 300 c.c., and barium chloride added so long as a precipitate is formed. This precipitate is washed with hot water and shaken with ether and hydrochloric acid in a

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[1] *Analyst*, 1881, v., 155.

Muter's tube. The ethereal solution containing the liberated fatty acids is made up to 100 c.c., an aliquot portion evaporated in a weighed flask, and dried until constant in weight. The results thus obtained are said to agree well with those obtained by Hehner's more tedious method.

Saponification Value of Insoluble Acids.—The fatty acids thus obtained are dissolved in pure alcohol and titrated with standard alcoholic alkali precisely as in the determination of the "free acid number" of an oil, etc. The quantity of potassium hydroxide ($KOH = 56{\cdot}1$) neutralised by the insoluble fatty acids obtained from 1,000 parts of original substance is conveniently referred to as the "*insoluble acid value*" of the oil, etc., examined.

The difference between the quantity of potassium hydroxide neutralised in the determination of the saponification equivalent (saponification value) and that thus found as the insoluble acid value, is obviously the potassium hydroxide equivalent to the acids present that are soluble in water. This difference is conveniently referred to as the "*soluble acid value*" of the oil, etc., tested. If the composition of these soluble acids is known or assumed (*e.g.*, regarding them as *butyric acid* in the case of butter fat), their weight is reckoned from the alkali neutralised as percentage on the original fat examined, and by adding this value to that calculated as above for the insoluble acids, the percentage of total acids present is obtained.

For example, suppose 2,500 grammes of butter fat to be saponified with 25 c.c. of semi-normal potassium hydroxide, and that on titrating the excess of alkali 4·9 c.c. are found to be unneutralised by the acids formed on saponification; then the total acids formed are equivalent to 25 − 4·9 = 20·1 c.c. of semi-normal alkali, or 10·05 c.c. of normal alkali. Hence the *total acid value*, or *saponification value*, is

$$\frac{10{\cdot}05}{2{,}500} \times 56{,}100 = 225{\cdot}5,$$

and the *saponification equivalent* is

$$\frac{2{,}500}{10{\cdot}05} = 248{\cdot}8.$$

After separation of the insoluble fatty acids, these are found to weigh 2·187 grammes, and to neutralise 16·6 c.c. of semi-normal alkali = 8·3 c.c. of normal alkali; hence the *insoluble acid value* is

$$\frac{8{\cdot}3}{2{,}500} \times 56{,}100 = 186{\cdot}25;$$

the percentage of insoluble fatty acids (*Hehner value*) is

$$\frac{2{,}187}{2{,}500} \times 100 = 87{\cdot}48;$$

and their *average equivalent weight* is

$$\frac{2{,}187}{8{\cdot}3} = 263{\cdot}5;$$

i.e., 1 c.c. of normal alkali neutralises 263·5 milligrammes of the mixed acids. Since the total acids neutralise 10·05 c.c. of normal alkali, and the insoluble acids 8·3 c.c., the difference = 1·75 c.c. represents the soluble acids. This corresponds with the *soluble acid value*

$$\frac{1 \cdot 75}{2{,}500} \times 56{,}100 = 39 \cdot 3.$$

If it be assumed that the soluble acids are essentially butyric acid (equivalent = 88), 1 c.c. of normal alkali will neutralise 88 milligrammes, and consequently 1·75 c.c. will neutralise 154 milligrammes = 6·16 per cent. of the 2,500 grammes of butter fat employed. Hence the total percentage of fatty acids formed on saponification is

Insoluble acids (Hehner value), ...	87·48
Soluble acid (reckoned as butyric acid), . . .	6·16
Total, ...	93·64

The mean equivalent weight of the total acids is calculated thus—

Weight of insoluble acids, . . .	2,187	milligrammes.
„ soluble „ . . .	154	„
Total, ...	2,341	„

Since these neutralise 20·1 c.c. of semi-normal alkali, equivalent to 10·05 c.c. of normal alkali, the mean equivalent weight is

$$\frac{2{,}341}{10 \cdot 05} = 232 \cdot 9.$$

Soluble Fatty Acids.—The soluble acids may also be directly estimated by employing a known quantity of standard acid to decompose the soap left after determination of the saponification equivalent, and determining the acidity of the aqueous filtrate, using phenol-phthalein as indicator. Thus, in the above case, suppose that 25 c.c. of semi-normal acid were used to decompose the soap, and that 8·4 c.c. of semi-normal alkali were neutralised by the aqueous filtrate; since the alkali present in the neutral soap represents 20·1 c.c., 25 − 20·1 = 4·9 c.c. of the acid used would remain unneutralised in the filtrate; whence, 8·4 − 4·9 = 3·5 c.c. of semi-normal acid, equal to 1·75 c.c. normal, would represent the soluble acids as before. In practice, this method is less accurate than the other, as the dilution of the fluid and the unavoidable absorption of carbonic acid from the air (which interferes with phenol-phthalein as an indicator) generally prevent so sharp a valuation being obtained.

With the exception of butter fat and allied animal fats, and coconut and palm-kernel oils, the amount of soluble acids present in ordinary oils and fatty matters is usually so small as to be negligible, so that the total acid value (saponification value) and the insoluble acid value are approximately the same—*i.e.*, the amount of alkali neutralised during saponification is practically identical with that neutralised subsequently by the liberated fatty acids, insoluble in water.

Correction for Anhydro Derivatives—*e.g.*, **Stearolactone.**—Certain distilled oleins, Turkey red oils, etc., contain *stearolactone*, the "inner" anhydride of hydroxystearic acid (p. 45). When this is heated with alcoholic potassium hydroxide it forms potassium hydroxystearate, which neutralises an equivalent of alkali ($C_{18}H_{36}O_2 = 300$); but when the resulting soap is decomposed by a mineral acid, stearolactone is reproduced. If the mixed fatty acids, etc., thus formed be titrated without heating, an insoluble acid value, corresponding with only the free fatty acids, will be indicated, the stearolactone not being converted into potassium hydroxystearate instantaneously in the cold; so that *an apparent existence of soluble fatty acids is indicated* by the difference between the saponification value obtained at first, and the value obtained during the titration of the free fatty acids—*i.e.*, their apparent neutralisation number. The deficiency, however, is made up if the neutralised fatty acids, etc., be heated with excess of alcoholic potassium hydroxide, and then titrated back, so as to determine the alkali neutralised by the formation of hydroxystearate. From the amount thus neutralised the stearolactone can be calculated, 1 c.c. of normal acid representing 282 milligrammes. Or the stearolactone may be dissolved out from the neutralised fatty acids by means of ether or petroleum spirit, and directly weighed.[1]

Corrections for Free Fatty Acids and for Unsaponifiable Matter.—If the substance examined contain free fatty acids or unsaponifiable matters the above methods require certain corrections. Thus, the value $E = \frac{w}{n}$, found as above for the saponification equivalent, does not represent the true equivalent of the glyceride or other compound ester present along with other matters, but only the *mean equivalent of all the substances present* (infinity in the case of non-saponifiable substances). If, as is usually the case, the unsaponifiable matters present are insoluble in water, the weight of substances obtained on saponifying and weighing the liberated fatty acids is too great by the amount of unsaponifiable substances present; and also by the weight of fatty acids originally present in the free state. These are determined as on pp. 166 to 177.

Suppose that a weight of substance, W, when saponified with alkali, neutralises n_1 c.c. of normal fluid; and, as the result of a previous titration before saponifying, suppose that n_2 c.c. represent the normal alkali equivalent to the free fatty acids present in the same weight, W, and that w_1 milligrammes is the weight of these fatty acids. Further, let the weight of unsaponifiable matter contained in W of substance be w_2 milligrammes. Then the saponifiable compound esters, glycerides, etc., present weigh $W - w_1 - w_2$ milligrammes; and the normal alkali neutralised by them on saponification is $n_1 - n_2$; hence the corrected saponification equivalent of the saponifiable matters free from impurities is

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[1] Benedikt, *Monatsh. f. Chem.*, xi., 71; *J. Soc. Chem, Ind.*, 1890, ix., 658.

$$E' = \frac{W - w_1 - w_2}{n_1 - n_2},$$

and the saponification value of these saponifiable matters free from impurities is

$$K' = \frac{n_1 - n_2}{W - w_1 - w_2} \times 56{,}100.$$

Sometimes it happens that during saponification products are formed that are insoluble in water and consequently rise to the surface when the resulting soaps are decomposed by a mineral acid so as to separate the fatty acids liberated on saponification—*e.g.*, in the case of cetacean oils, waxes, etc., where alcohols of high molecular weight, and not glycerol, are set free. In such cases, in order to obtain a correct valuation of the fatty acids, the quantity of such alcohols, etc., mixed with them must be determined.[1] This is usually conveniently effected by evaporating to dryness the alcoholic solution obtained when the weighed impure acids have been titrated, and dissolving out the alcohols, etc., with ether or petroleum spirit, so as to separate them from the soap. The filtered solution thus obtained is then evaporated, and the residue weighed and subtracted from the weight of crude fatty acids.

The equivalent weight of the fatty acids then will be

$$E = \frac{w - w'}{n};$$

where w is the weight in milligrammes of crude fatty acids, w^1 that of alcohols, etc., and n the number of c.c. of normal alkali neutralised.

Mean Equivalent of Fatty Acids Contained in Soap.—In the examination of soap it is often required to determine the mean equivalent of the fatty acids present in the form of potassium or sodium salts. In such cases the analytical methods used (Chap. XXI.) generally give the following data :—

Percentage of total alkali present (reckoned say as Na_2O), . = a
„ alkali not combined with fatty acids (so called "free alkali"), ... = b
„ free fatty acids formed on decomposition of the soap by mineral acids (together with unsaponified fat and neutral bodies, etc.), . . . = c
„ unsaponified fat and neutral bodies, etc., . . = d

Then 100 parts of material contain $a - b$ per cent. of alkali (reckoned as Na_2O) combined as soap with fatty acids, which soap again yields, on decomposition by a stronger acid, $c - d$ per cent. of fatty acids free from unsaponified fat and neutral bodies. The mean equivalent E

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[1] Owing to saponification changes occurring on keeping or during refining, it sometimes happens that considerable quantities of cetylic, dodecylic, etc., alcohols are contained *as such* in sperm oil, spermaceti, beeswax, and similar substances, in addition to those existing as compound esters ; as much as 40 to 50 per cent. has been found in extreme cases (*Allen* and *Thomson*).

of these fatty acids is then given by the proportion (31 being the equivalent of sodium oxide, Na_2O)

$$a - b : 31 :: c - d : E,$$

whence

$$E = \frac{c - d}{a - b} \times 31.$$

The fatty acids yielded by coconut oil have an average equivalent weight of not far from 200, whilst those from tallow, palm oil, and olive oil have much higher values, near 275. Still higher equivalent weights are possessed by the mixtures of acids yielded by castor oil (near 300) and oil of ben and rape oil (near 330), whilst cerotic and melissic acids from beeswax have equivalent weights of 410 and 452 respectively. Hence in many cases the numerical value of the equivalent weight of the fatty acids affords a useful indication as to the nature of the oils, etc., used in manufacturing the soap examined.

III. THE REICHERT VALUE.

Various natural oils and fats yield on saponification the alkali salts of mixtures of acids, some of which are readily volatile with the steam of water at ordinary pressure, and others practically non-volatile. *Reichert*[1] based on this a useful method for the detection of foreign fatty matter (oleomargarine, etc., in butter), these adulterants furnishing much smaller proportions of volatile acids. In practice, it is not convenient to continue the distillation until all the volatile acid present has passed over, so that a particular method of manipulation is employed, in order that an approximately constant fraction of the volatile acids may be distilled.

The following process is substantially that of Reichert :—2·5 grammes of the filtered fat are weighed into a small flask fitted with a cork, through which passes a short piece of glass tubing, and saponified by adding 5 c.c. of pure alcohol and 6 c.c. of a concentrated aqueous solution of potassium hydroxide (free from carbonate), and heating on the water-bath for a short time. After expelling all traces of alcohol the dry soap is dissolved in 70 c.c. of boiling water, and the fatty acids liberated by adding 5 c.c. of sulphuric acid of the right strength to neutralise the alkali. The liquid is then gently distilled[2] until exactly 50 c.c. have passed over. This distillate is filtered, the filter washed with boiling water, and the filtrate and washings titrated with decinormal solution of potassium or barium hydroxide. The number of c.c. required is the Reichert value.

Henriques[3] recommends the use of his method of cold saponification in the determination of the Reichert-Meissl value, with the object of saponifying every trace of the esters of volatile acids. Five grammes of the fat are dissolved in 25 c.c. of petroleum spirit and allowed to

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[1] *Zeit. anal. Chem.*, xviii., 68.

[2] To avoid bumping, pumice stone with platinum wire coiled round should be placed in the distilling vessel.

[3] *Zeit. angew. Chem.*, 1895, 721.

stand over-night in contact with 25 c.c. of a 4 per cent. alcoholic solution of sodium hydroxide. The next day the liquid is evaporated, the residue powdered, and the powder introduced into the distillation-flask with the quantity of water necessary for solution, and distilled with acid in the usual way.

By this method *Henriques* obtained Reichert Meissl values about 0·3 to 0·4 higher than by the older method.

Reichert Values of Certain Fats.—The following table, given by *Allen*,[1] represents the collected results obtained by himself and other analysts employing this method of manipulating:—

Substance, of which 2·5 grammes are used.	C.c. of Deci-normal Alkali neutralised by Distillate (filtered when necessary).	Percentage of KOH neutralised.
MILK FATS—		
Cow's butter, ...	12·5-15·2	2·80-3·41
Ewe's butter, ...	13·7	3·07
Goat's butter, ...	13·6	3·05
Porpoise's butter, . . .	11·3	2·51
ANIMAL & VEGETABLE OILS & FATS—		
Coconut oil,[2]	3·5-3·7	0·78-0·83
Palm kernel oil, ...	2·4	0·54
Palm oil, ...	0·8	0·18
Cacao butter, ...	1·6	0·36
Margarine and oleomargarine, .	0·2- 1·6	0·04-0·36
Whale oil, ...	3·7-12·5	0·83-2·80
Porpoise oil, ...	11-12	2·47-2·69
Sperm oil, ...	1·3	0·29
Bottlenose oil, ...	1·4	0·31
Menhaden oil, ...	1·2	0·27
Cod-liver oil, ...	1·1-2·1	0·24-0·47
Sesamé oil, ...	2·2	0·48
Cotton-seed oil, ...	0·3	0·07
Castor oil, ...	1·4	0·31

Reichert-Meissl Value.—Meissl[3] modified Reichert's test by using 5 grammes of fat instead of 2·5. The fat is saponified by adding to it 2 grammes of stick potassium hydroxide and 50 c.c. of 70 per cent. alcohol, and heating on the water-bath. The evaporated alcoholic soap is dissolved in 100 c.c. of water, and acidified with 40 c.c. of 10 per cent. sulphuric acid solution. 110 c.c. are slowly distilled off, of which 100 are filtered through a dry filter and titrated, the deci-normal alkali consumed being increased by one-tenth, to allow for the 10 c.c. not used. The results are more than double those obtained by Reichert's method of manipulation.

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[1] *Commercial Organic Analysis*, ii.

[2] By adding more water and continuing the distillation, a large amount of solid fatty acid, mostly insoluble in water (chiefly lauric acid), can be distilled over in the case of coconut oil.

[3] *Dingler's polyt. J.*, ccxxxiii., 229.

The following table, given by *Schädler*, represents the number of c.c. of deci-normal alkali neutralised by the volatile acids distilled off when the Reichert-Meissl test is employed (5 grammes of material used) :—

Name of Oil, &c.	C.c. of Deci-normal Alkali.	Name of Oil, &c.	C.c. of Deci-normal Alkali.
Arachis, . .	0·4	Nut (walnut), .	0·92
Almond, . .	0·55	Olive, . . .	1·5
Cotton-seed, . .	0·95	Palm, . . .	0·5
Coconut, . .	7·3	,, -kernel, . .	3·4
Cod-liver, . .	0·4	Poppy, . . .	0·6
Castor, . . .	4·0	Seal, . . .	2·6
Colza, crude, .	0·90	Sesamé, . .	1·2
,, refined, .	0·58	Sunflower, . .	0·5
Lard, . . .	1·10	Tallow (ox), . .	1·0
Linseed, . .	0·95	,, (sheep), .	1·2

Other Modifications of the Test.—Numerous other modifications of Reichert's mode of manipulating have been proposed by different chemists with the object of obtaining greater accuracy. *Wollny*[1] employs special precautions to avoid the presence of carbon dioxide in the distillate and eliminate its disturbing effect, and prescribes that the distillation (using 5 grammes of butter fat) should always last the same time, thirty minutes. Similarly, *Leffmann* and *Beam*[2] use a solution of sodium hydroxide in glycerol instead of alcohol, to diminish possible formation of volatile acids by the action of the alkali on the alcohol. Methyl alcohol is used by others for the same purpose. The official method of applying the test is described under *Butter*, Chap. XV.

Phosphoric acid was recommended by *Munier* as a substitute for sulphuric acid in the liberation of the fatty acids, but, according to *Cornwall*,[3] this modification gives too low results. *Kreiss* advocated the use of concentrated sulphuric acid for the saponification (*cf. Butter*).

Bondzynski and *Rufi*[4] describe a method which enables the Hehner and Reichert values to be determined in one operation. From 4 to 5 grammes of the fat are saponified with standard alcoholic potassium hydroxide, and the soap, after evaporation of the alcohol, dissolved in water, and treated with the exact quantity of hydrochloric acid equivalent to the alkali used. The liberated fatty acids are washed, dried, and weighed, and the filtrate and washings titrated with deci-normal alkali.

Reichert Value of Mixtures of Butter and Margarine.—Assuming that pure butter fat gives a Reichert-Wollny value = 27, and that the corresponding number for average margarine is 2, a sample of butter fat mixed with margarine and giving the number R will contain x per cent. of margarine, where

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[1] *Analyst*, 1887, xii., 203, from *Milch Zeit.*, 1887, Nos. 32-35.

[2] *Analyst*, 1891, xvi., 153.

[3] *Chem. News*, liii., 20.

[4] *J. Soc. Chem. Ind.*, 1890, ix., 44.

$$x = 100 \times \frac{27 - R}{25} = 4\,(27 - R).$$

The Reichert value of genuine butter, however, has been found to vary so greatly that too much reliance must not be placed on such calculations.

Total Amount of Volatile Acids.—The volatile acids thus indicated are usually considerably below the total amount actually present. According to *Allen*, the deficiency is somewhere about one-fifth in the case of butter fat, and presumably in about the same proportion in other cases. When a nearer approximation to the total volatile acid present is required, water must be added to the residue in the flask and distillation recommenced, and so on as long as acid vapours pass over. Or, more conveniently, steam may be blown through the liquid from a separate boiling vessel, when, as *Meyer* has shown, a Reichert value higher by 25 per cent. can be obtained in the first distillation.

Goldmann[1] continues the distillation in a current of steam until only 0·5 c.c. of N/10 alkali are necessary for the neutralisation of 100 c.c. of distillate. His process, however, is very tedious, thirteen distillations being required to expel the volatile acids from butter fat.

Extended Reichert Process.—It has been proposed to extend the Reichert-Meissl process so as to include the amount of volatile insoluble fatty acids obtained under the same conditions.

Reychler[2] adds 50 c.c. of alcohol to the distillate, and, if necessary, a little ether, and titrates the solution in the usual way. The ratio between the total volatile acids and the soluble volatile acids varies greatly in different fats. Thus, in the case of butter, it is 0·91, whilst with coconut oil it is 0·33.

Wauters[3] recommends an analogous method:—Five grammes of the fat are saponified, the soap dissolved in 150 c.c. of boiling water, 50 c.c. of 5 per cent. sulphuric acid introduced, and 100 c.c. distilled in thirty to thirty-five minutes. The distillation is repeated after the addition of 100 c.c. of boiling water. The two distillates are filtered, and 50 c.c. of each titrated. The filters are then washed with 50 c.c. of alcohol and the washings mixed with the other 50 c.c. of the filtrates, and again titrated.

In this way the following results were obtained :—

Fat.	Soluble Volatile Acids.			Insoluble Volatile Acids.		
	First Distillation	Second Distillation	Total.	First Distillation	Second Distillation	Total.
Coconut oil,	7·10	4·30	11·40	7·85	7·55	15·4
Cacao butter,	0·10	0	0·10	0·25	0·15	0·4
Butter, . .	22·4	5·4	27·8	0·6	0·3	0·9

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[1] *J. Soc. Chem. Ind.*, 1888, vii., 238, 349.

[2] *Bull. Soc. Chim.*, 1901, xxv., 142.

[3] *Bull. de l'Ass. belge Chim.*, 1901, xv., 25 and 131.

For further particulars of the application of these methods to the analysis of butter see Chap. xv.

Kirschner [1] extended the Reichert process in such a way as to distinguish between the amounts of caprylic and butyric acids, his process being based upon the fact that silver caprylate is insoluble, whilst silver butyrate is soluble in water.

After titration, the Reichert distillate is shaken with 0·5 gramme of silver sulphate and filtered after standing for 30 minutes. The filtrate is distilled under specified conditions, the distillate filtered, and 100 c.c. titrated with N/10 barium hydroxide solution.

The results are expressed in the number of c.c. required by 5 grammes of the fat, and the percentage of butter fat present is calculated by means of the formula—

$$4{\cdot}319\,S - 0{\cdot}456\,R - 2{\cdot}15,$$

and the percentage of coconut oil by the formula—

$$7{\cdot}42\,R - 8{\cdot}116\,S - 3{\cdot}57,$$

where R represents the Reichert-Meissl value, and S the results obtained by Kirschner's process.

THE POLENSKE VALUE.

This affords a measure of the proportion of insoluble fatty acids which distil with the soluble fatty acids in the determination of the Reichert value.

In order to obtain concordant results, it is essential that the details of the measurements of the apparatus and of the method of working given by *Polenske* [2] should be closely followed, since the figures obtained do not represent the definite amount of insoluble volatile acids, but only that proportion obtained under the prescribed conditions (see *Butter*).

The insoluble volatile fatty acids left on the filter and in the condenser after determining the Reichert-Meissl value are dissolved in alcohol, and the solution titrated with N/10 barium hydroxide solution, with phenol-phthalein as indicator. The number of c.c. required is the Polenske value.

Since coconut oil is much richer in insoluble volatile fatty acids than butter fat, it will show a much higher *Polenske* value. For example, *Polenske* found that four samples of coconut oil with Reichert-Meissl values of 6·8 to 7·7 gave Polenske values of 16·8 to 17·8, whereas in the case of 31 samples of butter fat, with Reichert-Meissl values of 23·3 to 30·1, the Polenske values were only 1·5 to 3·0.

Revis and *Bolton* [3] confirm the value of this method and give the following table of Reichert-Meissl and corresponding Polenske values :—

Reichert-Meissl value,	32	31	30	29	28	27	26	25	24	23
Polenske value, . .	3·5	3·2	3·0	2·9	2·7	2·4	2·0	1·8	1·7	1·6

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[1] *Zeit. Nahr. Genussm.*, 1905, ix., 65 (*Analyst*, 1905, xxx., 205).

[2] *Zeit. Nahr. Genussm.*, 1904, vii., 273 (*Analyst*, 1904, xxix , 154).

[3] *Analyst*, 1911, xxxvi., 333.

In their experience, if a butter fat gives a Polenske value exceeding by 0·5 c.c. the figure corresponding with the Reichert-Meissl value the presence of coconut or palm-kernel oil is indicated.

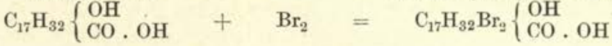
IV. BROMINE AND IODINE ABSORPTION.

Organic compounds containing a group of the character $-\mathrm{C}R=\mathrm{C}S-$ tend to combine with two atoms of a given halogen such as bromine or iodine, forming a group of formula $-\mathrm{C}R\mathrm{Br}-\mathrm{C}S\mathrm{Br}-$, or $-\mathrm{C}R\mathrm{I}-\mathrm{C}S\mathrm{I}-$. Accordingly, organic acids thus constituted are capable of uniting directly with halogens to an extent dependent on the number of times that such "doubly linked" carbon groups occur. Thus oleic and ricinoleic acids, which contain one such doubly-linked pair of carbon atoms, unite with Br_2.

Oleic Acid. Dibromostearic Acid.

$$\mathrm{C_{17}H_{33} \,.\, CO \,.\, OH} \quad + \quad \mathrm{Br_2} \quad = \quad \mathrm{C_{17}H_{33}Br_2 \,.\, CO \,.\, OH}$$

Ricinoleic Acid. Dibromohydroxystearic Acid.



$$\mathrm{C_{17}H_{32}}\begin{cases}\mathrm{OH}\\ \mathrm{CO \,.\, OH}\end{cases} \quad + \quad \mathrm{Br_2} \quad = \quad \mathrm{C_{17}H_{32}Br_2}\begin{cases}\mathrm{OH}\\ \mathrm{CO \,.\, OH}\end{cases}$$

Similarly, linolic acid combines with Br_4, as it contains *two*[1] such doubly-linked pairs of carbon atoms.

Linolic Acid. Tetrabromostearic Acid.

$$\mathrm{C_{17}H_{31} \,.\, CO \,.\, OH} \quad + \quad \mathrm{Br_4} \quad = \quad \mathrm{C_{17}H_{31}Br_4 \,.\, CO \,.\, OH}$$

Whilst linolenic acid, containing 3 such pairs[2] unites with Br_6—

Linolenic Acid. Hexabromostearic Acid.

$$\mathrm{C_{17}H_{29} \,.\, CO \,.\, OH} \quad + \quad \mathrm{Br_6} \quad = \quad \mathrm{C_{17}H_{29}Br_6 \,.\, CO \,.\, OH}$$

In certain cases, the bromine addition products thus formed are crystallisable, and thus afford the means of separating organic acids from one another (*cf.* Chap. VI.). In any case, by determining the quantity of halogen fixed by a given acid or mixture of acids, useful information is often obtained as to the nature of the fatty acids present. For instance, if a mixture of stearic and oleic acids absorbed, say, 45 per cent. of its weight of iodine, since stearic acid takes up no iodine, and oleic acid 90 per cent. of its weight, it would result that the mixture contained the two acids in approximately equal quantities. Methods for the determination of the amount of oleic acid in mixtures of this kind are of considerable practical utility; in particular, the author (*Alder Wright*) found the method useful in determining the proportion of oleic acid contained in the "stearine" used for candle-making.

Precisely the same remarks also apply to the glycerides of the fatty acids, with the sole difference that their combination with halogens generally takes place more slowly than in the case with the fatty acids contained, or with the parent hydrocarbons of these fatty acids.

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[1] Or possibly a trebly-linked pair of carbon atoms, forming the group $-\mathrm{C}\equiv\mathrm{C}-$, which, by uniting with Br_4, produces a group of formula $-\mathrm{CBr_2}-\mathrm{CBr_2}$.

[2] Or possibly one trebly-linked pair, and one doubly-linked pair.

As far back as 1857, attempts to utilise the reaction with bromine for the practical discrimination of fats were made by *Cailletet*, and subsequently by *Allen*, *Mills*, and others; but although in certain cases useful results are thus obtainable, in practice it has been found that the use of iodine is often preferable, more especially when applied in the modified form devised by Hübl (*vide infra*), in which mercuric chloride and iodine are dissolved in alcohol, and the compound solution allowed to act on the fat, or in Wijs' iodine chloride method (*infra*). There is usually some degree of substitution as well as addition of bromine. This varies with different oils, and is taken into account in M'Ilhiney's method of determining the bromine absorption (*infra*).

Bromine Absorption Processes.

Earlier Methods.—The bromine absorption process, as improved by *Mills* and *Snodgrass*,[1] and *Mills* and *Akitt*,[2] consists in dissolving 0·6 to 0·7 per cent. of bromine in carbon bisulphide, or preferably carbon tetrachloride, and adding this to a solution of a weighed quantity of oil in the same solvent, until no more combination takes place. In the earlier experiments with carbon bisulphide a slight excess of bromine was added, and the colour, after standing fifteen minutes, compared with that of a known amount of bromine dissolved in carbon bisulphide, so as to obtain a colorimetric valuation of the excess; or the excess of bromine was estimated by adding potassium iodide and titrating with thiosulphate. In the later experiments with carbon tetrachloride, about 0·1 gramme of oil was dissolved in 50 c.c. of tetrachloride, an excess of bromine solution added, and after fifteen minutes the excess titrated back either by the coloration method,[3] with iodide and thiosulphate, or with a standard solution of β-naphthol in carbon tetrachloride.

The table opposite gives the results of a number of determinations thus made.

M'Ilhiney's Method.—*M'Ilhiney*[4] described a method of determining the bromine absorption, which he afterwards simplified[5] by adopting the iodometric method of *Schweizer* and *Lungwitz*[6]:—A weighed quantity of the oil is dissolved in 10 c.c. of carbon tetrachloride in a stoppered bottle and 20 c.c. of $\frac{1}{3}$ N solution of bromine in carbon tetrachloride introduced. After one to two minutes, 20 to 30 c.c. of potassium iodide solution (1 : 10) are added, the bottle shaken

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[1] *J. Soc. Chem. Ind.*, 1883, ii., 435.

[2] *Ibid.*, 1884, iii., 366.

[3] When the oil is yellow, as with certain fish oils, the redness due to excess of bromine is best examined by viewing through a solution of potassium chromate.

[4] *J. Amer. Chem. Soc.*, 1894, xvi., 275.

[5] *Ibid.*, 1899, xxi., 1084.

[6] *J. Soc. Chem. Ind.*, 1895, xiv., 130.

Substance.	Percentage of Bromine absorbed.	Specific Gravity at 11°-12°.	Melting Point.	Remarks.
			°C.	
Almond oil, . .	26·27	0·9168	...	Expressed from bitter almonds.
,, . .	53·74	0·9154	...	Expressed from sweet almonds; yellower.
Beeswax, . .	0·54	...	63·9	English, a few months old; very yellow.
,, . .	0	...	63·2	Scotch, 8 years old; pale.
,, . .	0	...	62·9	,, 2 ,, yellow.
,, . .	0	...	63·3	,, 1 ,, ,,
Ben oil, . . .	52·95	0·9198	...	Much solid fat.
,, . . .	50·89	0·9161	...	No solid fat.
Carnauba wax, .	33·50	...	84·1	... ...
Cod-liver oil, . .	83·12	0·9269	...	Scotch, 7 years old; rancid; clear portion used; 1 hour's absorption.
,, . .	84·03	0·9[illegible]92	...	Norwegian, refined, 2 years old.
,, . .	82·94	0·9257	...	Japanese, 2 years old.
,, . .	81·61	0·9277	...	Scotch, 2 years old.
,, . .	86·69	0·9281	...	Crude, from liver refuse; a few months old.
,, . .	83·01	0·9318	...	Norwegian, 1 year old.
,, . .	82·07	0·9278	...	Scotch, ,,
Croton oil, . .	46·66	0·9441	...	20 hours' absorption.
Eucalyptus oil, .	94·09	0·8691	...	... ...
Horse fat, . .	35·67	...	...	Pasty; well mixed.
Japan wax, . .	2·33	...	50·5	... ...
,, (another sample),	1·53	...	50·8	... ...
Java-nut oil, . .	30·24	...	...	... ...
Ling-liver oil, .	82·44	0·9295	...	2 years old; 1 hour's absorption.
Maize-germ oil, .	74·42	0·9262	...	4 years old.
Mustard-seed oil, .	46·15	0·9152	...	East Indian.
Myrtle wax, . .	6·34	...	44·3	... ...
Neat's foot oil, .	38·33	0·9147	...	Thick.
Niger-seed oil, .	35·11	0·9244	...	... ...
Olive oil, . .	59·34	0·9266	...	Thick brown; "best sulphocarbon."
,, . .	60·61	0·9382	...	Thinner greener; "low quality sulphocarbon."
Palm oil, . .	35·44	...	...	Crude old Calabar.
,, . .	34·96	...	...	,, Lagos.
Peach kernel oil, .	25·40	0·9175	..	... ...
Poppy oil, . .	56·54	0·9244	...	Turbid; filtered.
Resin (common), .	112·70	...	...	Light colour.
Seal oil, . . .	57·34	0·9241	...	Pale; 1 hour's absorption.
,, . . .	59·92	0·9216	...	Dark.
Sesamé oil, .	47·35	0·9250	...	... ...
Shark-liver oil, .	84·36	0·9293	...	A few months old; 1 hour's absorption.
Sunflower oil, .	54·32	0·9391	...	Colourless; about 16 years old.
Whale oil, . .	30·92	0·9199	...	Norwegian white whale; very thick.
,, . .	48·69	0·8780	...	Bottlenose whale.

to insure the absorption of the bromine and hydrobromic acid, the iodine titrated with N/10 thiosulphate solution, and the bromine addition value calculated from the result. After the titration, 5 c.c. of a neutral 2 per cent. solution of potassium iodate solution are introduced and the liberated iodine corresponding to the hydrobromic acid is titrated and calculated into the bromine substitution value.

In order to prevent any loss of bromine or hydrobromic acid, a piece of wide indiarubber tubing is slipped over the neck of the bottle so as to form a well round the stopper. The potassium iodide solution is poured into the well, and the stopper slightly opened, preferably after the bottle has been cooled in ice, so as to create a partial vacuum. The following results, among others, were thus obtained :—

Oil.	Hübl Value.	Bromine Value Calculated from I. Value.	Bromine Absorbed.	Bromine Addition Value.	Bromine Substitution Value.	Calculated Bromine Value Divided by Br. Addition Value.
Raw linseed, av. of 7, .	183·8	115·7	112·0	106·6	2·7	1·083
Boiled ,, ,, 8, .	...	..	109·5	103·0	3·2	...
"Java" boiled rosin, .	73·3	46·2	101·9	8·3	46·8	5·685
Menhaden, av. of 3, .	174·9	110·2	110·6	95·6	7·5	1·154
Maize, av. of 3, . .	...	...	75·8	72·9	1·5	...
Cotton-seed, . . .	...	...	65·8	62·2	1·8	...
Turpentine, . . .	...	...	266·1	166·1	50·0	...
Coconut, . . .	...	...	5·36	4·7	0·33	...
Tallow, . . .	...	...	24·0	21·48	1·26	...
Hard paraffin, . .	...	...	3·55	1·43	1·06	...
Black rosin, . . .	...	...	135·4	5·4	65·0	...

The differences between 1·000 and the figures in the last column represent the degree of substitution which occurred in the determination of the Hübl value.

Vulté and *Logan* [1] have made comparative determinations of the iodine and bromine values of various oils, the bromine figures being determined by M'Ilhiney's method, with the exception that thirty minutes were allowed before the titration. Hübl's method was employed for the iodine values, the flasks being left in the dark for twenty-four hours before titrating.

In the following table the oils are grouped into classes according to the increasing divergence between the bromine and iodine figures. The oils in the first class show but little difference, and either value may be determined. In the case of the rape oil there was apparently more substitution with iodine than with bromine, possibly owing to the longer time of action of the former :—

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[1] *J. Amer. Chem. Soc.*, 1901, xxiii., 156.

Oil.	Iodine Value (*Hübl*).	Iodine Value Calculated from Bromine Value.	Difference of Averages.	Difference of Nearest Figures.
I. Olive, . .	79·70-80·40	80·31	0·26	0·09
Cotton-seed, .	97·50	97·41- 97·00	0·295	0·09
Poppy, . .	127·98-128·55	128·37	0·55	0·28
Linseed, . .	155·12-155·52	154·80	0·52	0·32
Sweet almond, .	90·53- 89·64	90·20- 89·64	1·08	0·33
Earth-nut, .	100·71-100·76	101·26	0·523	0·50
Whale, . .	128·00	127·45-127·38	0·585	0·50
Lard, . .	76·90- 77·36	76·03- 75·88	1·22	0·96
II. Sperm, . .	79·95- 79·76	82·39- 82·08	2·422	2·13
III. Rape, . .	103·69-103·37	99·03- 98·56	4·60	4·17
Castor, . .	86·32- 87·15	78·74- 78·71	8·01	7·58
IV. Seal, . . .	93·31- 93·99	103·09-103·74	9·765	9·10
Cod-liver, . .	122·09-122·79	132·86-132·18	10·08	9·39
Menhaden, .	176·05-175·65	186·94-186·86	10·825	10·36
V. Rosin, . .	59·67-58·95	10·60- 10·26	48·845	48·35

It is suggested by *Vulté* and *Logan* that the ratio between the two values may give useful indications in certain cases—*e.g.*, of the presence of menhaden oil in linseed oil.

Of these fifteen oils only six showed any marked degree of substitution with bromine. The average values given by these were as follows :—

Oil.	Total Bromine Absorption.	Addition Figure.	Substitution Figure.
Cod-liver, . .	84·91	84·305	0·605
Menhaden, . .	120·15	118·905	1·245
Sweet almond, .	59·345	57·20	2·145
Sperm, . . .	54·585	52·31	2·27
Castor, . . .	52·71	50·08	2·63
Rosin, . . .	108·90	6·605	102·345

Rowland Williams[1] finds that in many cases it is a matter of indifference whether the bromine or iodine value be determined, but in the case of other oils, notably linseed, he has obtained very discordant results between the iodine values as determined by Wijs' method and calculated from the bromine value. He considers that with linseed, and possibly other highly unsaturated oils, the full bromine absorption will only be complete when a very large excess of bromine is added, if then. He advocates allowing the flask to stand for fifteen minutes before the titration.

The following table shows the comparative results which he has obtained with different oils :—

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[1] *J. Soc. Chem. Ind.*, 1900, xix., 300.

Oil or Fat.	Iodine Value (*Wijs*).	Bromine Value Calculated from Iodine.	Bromine Value, Determined.	Bromine Addition Value.	Bromine Substitution Value.
Coconut oil, . .	9·58	6·05	5·09	...	...
Tallow, . . .	31·61	19·98	19·84	17·86	0·99
Butter fat, . .	34·55	21·84	21·22	20·78	0·22
Lard, . . .	63·87	40·36	40·63	...	...
Castor oil, . .	83·41	52·71	50·69	47·21	1·74
Rape oil, . . .	103·62	65·49	65·26	64·16	0·55
Cotton-seed oil, .	108·89	68·82	65·82	64·52	0·65
Maize oil, . . .	124·48	78·67	75·12	73·38	0·87
Japanese wood oil, .	158·42	100·12	95·83	92·33	1·75
Menhaden oil, . .	183·11	115·72	110·51	104·79	2·86
Linseed oil (9 samples), .	186·97 to 202·49	118·16 to 127·97	109·31 to 122·28	102·19 to 116·74	1·68 to 3·56

Gravimetric Method.—*Hehner*[1] has devised the following gravimetric method, which gives reliable results in the case of many oils:—From 1 to 3 grammes of the fat are dissolved in chloroform in a small wide-mouthed flask of known weight. The bromine is then expelled on the water-bath, a little more chloroform added, and the flask again heated and finally dried in an air-bath at 125° C. until constant in weight. The increase in weight multiplied by 1·587 gives the iodine value.

The following results were thus obtained among others:—

	Iodine Value (*Hübl*).	Iodine Value Calculated from Bromine.
Olive oil, ...	80·3	81·5
Lard, ...	65·7	64·4
Maize oil, ...	122·0	123·2
Butter fat, ...	34·0	34·3
Castor oil, ...	83·0	69·5
Boiled linseed oil, . . .	132·5	159·5

Lewkowitsch,[2] on repeating Hehner's experiments, obtained a satisfactory agreement between the gravimetric bromine and the Hübl values of olive and rape-seed oils, but with castor oil, linseed oil, cotton-seed oil, and oleic acid, the discrepancy between the two values was very great.

Hehner replied to these criticisms in a further paper.[3]

On the other hand, *Williams*[4] speaks in the highest terms of the accuracy and value of the gravimetric method as applied to raw linseed oil, and considers it in many cases more convenient and reliable than the Hübl volumetric process.

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[1] *Analyst*, 1895, xx., 49.

[2] *J. Soc. Chem. Ind.*, 1896, xv., 859.

[3] *J. Soc. Chem. Ind.*, 1897, xvi., 88.

[4] *Analyst*, 1895, xx., 277.

Jenkins[1] finds that the gravimetric figures obtained after drying for three and five hours at 97° C. agree fairly well with the Hübl and bromine thermal values, but that the brominated products are not quite stable, so that it is difficult to ascertain the point at which the weight is sufficiently constant.

His results are shown in the following table :—

Oil.	Iodine Values.					
	Hübl.	Bromine-thermal.	Bromine-Gravimetric.			
			Dried at 97° C.		Dried at 125° C.	
			3 hours.	5 hours.	3 hours.	5 hours.
Rape, . . .	100·2	98·6	99·8	99·0	96·8	95·5
Raw linseed, . .	174·3	173·9	171·1	168·8	161·8	156·9
Boiled linseed, . .	166·6	166·7	169·9	166·2	157·5	154·9
Castor, . . .	84·1	83·8	88·8	86·9	80·0	77·2

The Bromine Thermal Process.—*Hehner* and *Mitchell*[2] showed that the action of bromine upon oils and fats was practically instantaneous, and that the amount of heat evolved was proportional to the degree of unsaturation as measured by the iodine absorbed in Hübl's process.

Their first experiments were made in a test-tube surrounded by cotton-wool in a beaker, but subsequently a small vacuum-jacketed tube was employed, which gave results about 2° higher.

The bromine, oil, and solvent were all brought to the same initial temperature. One gramme of the oil was then dissolved in 10 c.c. of chloroform in the tube and the temperature taken with a standard Jena thermometer graduated in fifths of a degree. One c.c. of bromine was introduced, the liquid stirred with the thermometer, and a note made of the highest temperature attained.

In order to take up 1 c.c. of bromine without inconvenience, a 1-c.c. pipette was used, connected at the upper end with a narrow tube filled with caustic lime, and having an asbestos plug at each end. Suction was applied to the end of this tube, and all bromine vapours retained by the lime.

For the particular apparatus and method of working employed, the rise of temperature multiplied by 5·5 gave the calculated iodine value. Of course, the factor will be different with other tubes and thermometers, and must be determined by taking the bromine-thermal rise of a number of fresh oils and fats of which the exact iodine values have been ascertained.

The following table gives the results thus obtained by *Hehner* and *Mitchell* :—

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[1] *J. Soc. Chem. Ind.*, 1897, xvi., 193.

[2] *Analyst*, 1895, xx., 146.

Oil or Fat.	Rise of Temperature with Bromine. °C.	Hübl Value.	Calculated Iodine Value.
Lard,	10·6	57·15	58·3
,,	10·4	57·13	57·2
,,	11·2	63·11	61·6
,,	11·2	61·49	61·6
,,	11·8	64·69	64·9
,,	11·8	63·96	64·9
,,	10·2	57·15	56·1
,,	10·4	57·8	57·2
,,	9·0	50·38	49·5
,,	11·0	58·84	60·5
,, + 10 per cent. cotton oil,	11·6	64·13	63·8
,, fatty acids,	10·4	59·6	57·2
,, ,,	11·0	59·15	60·5
Mutton fat (kidney),	8·1	44·48	44·5
,, ,, (flare),	7·6	39·7	41·8
Butter,	6·6	37·07	36·3
,,	7·0	38·60	38·5
,, fatty acids,	6·2	36·5	34·1
Almond oil,	17·6	96·64	96·68
Olive oil,	15·0	80·76	82·5
Maize oil,	21·5	122	118·2
Cotton oil,	19·4	107·13	106·7
Castor oil,	15·0	83·77	82·5
Linseed oil,	30·4	160·7	167·2
,, ,,	31·3	154·9	172
Rape oil,	18·4	88·33	101·2
,,	17·6	77·2	96·8
Cod-liver oil,	28	144·03	140
Oil sent as olive oil,	19	108·5	104·5
,, ,, ,,	19·2	105·7	105·6
,, ,, ,,	18·9	105·7	103·9

Jenkins[1] observed a general agreement between the Hübl value and the iodine value calculated from the bromine thermal figure in the case of—Neat's foot, olive, bottlenose, castor, rape, ravison, seal, and raw and boiled linseed oils; whilst Japanese wood and blown cotton-seed and rape oils formed pronounced exceptions. Thus—

Oil.	Hübl Value.	Iodine Value calculated from Bromine Thermal Figure.
Blown rape (sp. gr. 0·9621),	55·3	74·1
Blown cotton-seed (sp. gr. 0·9639),	62·2	78·1
Japanese wood (sp. gr. 0·9385),	165·7	133·4

The higher values calculated from the bromine reaction here are evidently due to a considerable amount of substitution taking place on adding bromine to oil containing such oxidised fatty acids.

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[1] *J. Soc. Chem. Ind.*, 1897, xvi., 194.

Archbutt[1] considers the bromine thermal process as a most valuable auxiliary method where a large number of samples of oil are to be examined. He shows that the method yields reliable results with tallow, olive oil, rape oil, and raw linseed oil, and also that it makes practically no difference whether the bromine be anhydrous or saturated with water.

Wiley[2] recommends certain modifications of the test. The bromine is dissolved in the chloroform in the proportion of 1 to 4, and the solution placed in an Erlenmeyer flask with a side-tubulure on which is fixed a rubber bulb. A pipette is passed through the cork of the flask, and the bromine solution can be blown up into this pipette by compressing the bulb.

Another modification proposed by Wiley is to dissolve the fat in chloroform and to use aliquot portions of the solution for the test.

He has also tried carbon tetrachloride as a solvent, and found it to give results slightly lower than in the case of chloroform.

In the present writer's opinion, these modifications offer no advantages over the original method, for there is no difficulty in manipulating the bromine with a lime-tube guard on the pipette, and duplicate tests can be rapidly made by weighing out fresh portions of the fat.

Moreover, as *Archbutt* has pointed out, the bromine vapour must speedily destroy the india-rubber inside the bulb-compressor on the flask.

Specific Bromine Thermal Reaction.—In order to render the results obtained with different calorimeters comparable, *Gill* and *Hatch*[3] suggest referring the rises in temperature to a standard, as in Thomson and Ballantyne's method of applying the Maumené test. Finding that sublimed camphor can be obtained in a sufficiently pure state, they adopt this as their standard material. The bromine thermal value of the camphor is determined in the apparatus and by the method chosen, and the rise in temperature on brominating different oils divided by this number, thus giving a "specific temperature reaction."

The following results were obtained by a method substantially the same as Wiley's modification (*supra*). The factor 17·18 was found by dividing several of the Hübl values by this specific temperature :—

Oil.	Specific Temperature Reaction.	Iodine Value.	
		Calculated.	Determined (*Hübl*).
Neat's foot, . . .	3·286	56·5	59·1
Tallow, ...	3·348	57·4	57·2
Prime lard, . . .	3·715	63·8	63·8
Sperm.	4·191	72·1	73·2
No. 1 lard, . . .	4·096	70·3	78·9
Olive, ...	4·762	81·8	82·0
Cotton-seed, . . .	5·667	97·3	103
Maize, ...	6·381	109·5	107·8
Cod, ...	8·002	137·4	135·0
Linseed, ...	9·049	155·6	160·0

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[1] *J. Soc. Chem. Ind.*, 1897, xvi., 309.

[2] *J. Amer. Chem. Soc.*, 1896, xviii., 378.

[3] *J. Amer. Chem. Soc.*, 1899, xxi., 27.

Marden[1] has described a modification of the method, in which the heat of bromination is expressed in calories per gramme of oil, and the relationship of the values to the iodine values of a number of typical oils is given. Any pronounced difference between the calculated and determined iodine values must be attributed to there being a greater degree of substitution by the bromine than the iodine.

Iodine Processes.

Absorption of Free Iodine.—The absorption of free iodine by fats and oils is considerably slower than the absorption of bromine, and although the use of a solution of iodine was discarded by *Hübl*, several attempts have since been made on the same lines.

Thus *Gannter*[2] recommended a solution of iodine in carbon tetrachloride; but even after standing for fifty hours the amount of halogen absorbed was considerably less than in the Hübl method.

Hübl's Method.[3]—An alcoholic solution of mercuric chloride and iodine in pure 95 per cent. alcohol is prepared by dissolving 50 grammes iodine in one litre of spirit, and 60 grammes corrosive sublimate in another litre, filtering the latter if necessary, and mixing the two solutions. Preferably they are kept apart and only mixed a day or two before use.[4] The compound solution rapidly loses strength (as regards free iodine) if fusel oils are present in the alcohol, methylated spirit being wholly inadmissible. In any case the liquid should be allowed to stand at least a day before use, so that any small quantity of iodine-consuming impurities may be eliminated as far as possible; and the actual iodine strength must be determined from time to time to allow for depreciation.

From 0·2 to 0·3 gramme of drying oils, 0·3 to 0·4 gramme of non-drying oils, or 0·8 to 1·0 gramme of solid fats, is dissolved in 10 c.c. of pure chloroform (*i.e.*, containing no iodine-consuming impurity), and to the solution 30 or 40 c.c. of iodine solution added, more being introduced if on standing for some time the brown colour lightens materially. Enough solution must be added in all to give a large excess of free iodine when the action is complete after several hours' standing.

After the addition of 10 to 15 c.c. of a 10 per cent. solution of potassium iodide with about 150 c.c. of water, the excess of iodine is titrated with a solution of sodium thiosulphate (about 24 grammes per litre) previously standardised on pure sublimed iodine or potassium bichromate, a little starch paste being used as an indicator towards the end of the titration.

As the excess of iodine is dissolved partly in the aqueous liquor and partly in the chloroform, the whole must be well agitated. Unless

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[1] *J. Ind. Eng. Chem.*, 1916, viii., 121.

[2] *J. Soc. Chem. Ind.*, 1893, xii., 717.

[3] *Dingler's polyt. J.*, 1884, 253, 281; Abst. in *J. Soc. Chem. Ind.*, 1884, iii., 641.

[4] According to *Saytzeff*, mercuric bromide is preferable to mercuric chloride, the solution being more stable.

a considerable excess of free iodine is present, and the whole allowed to stand for several hours, defective results are apt to be obtained with glycerides, as the assimilation of iodine with these bodies is not always rapid; free fatty acids combine with iodine more quickly.

The author considered it a good rule to use an excess of iodine approximately equal to the amount absorbed,[1] and to allow the whole to stand until the next day before titration of the uncombined iodine; one or more blank experiments being simultaneously arranged to allow for possible depreciation in strength of the iodine solution during the period; this lengthened time is more especially necessary in the case of oils absorbing large amounts of iodine. Thus the following figures illustrate this point (*Thomson* and *Ballantyne*):—

Time of Absorption.	Iodine Number Found.	
	Seal Oil.	Linseed Oil.
2 hours.	136·6	175·5
4 ,,	140·8	179·7
6 ,,	145·1	184·1
8 ,,	145·8	187·7
18 ,,	145·8	187·7

Similar figures have been published by various other observers in the case of glycerides absorbing large proportions of iodine, whereas, with free fatty acids and glycerides absorbing but little iodine, the reaction is ordinarily found to be practically complete in three hours.

When the iodine absorption of free fatty acids is to be determined, it is unnecessary to dissolve them in chloroform; the alcoholic mercury-iodine solution may be added directly to the weighed fatty acids, previously thinned a little by warming with a small quantity of pure alcohol. The following table represents the amounts of iodine theoretically taken up by 100 parts of the several acids and their respective triglycerides:—

Name.	Formula.	Iodine Absorption.	
		Acid.	Glyceride.
Hypogæic acid, ...	$C_{16}H_{30}O_2$	100·00	95·25
Oleic acid, ...	$C_{18}H_{34}O_2$	90·07	86·20
Erucic acid, ...	$C_{22}H_{42}O_2$	75·15	72·43
Ricinoleic acid, ...	$C_{18}H_{34}O_3$	85·24	81·76
Linolic acid, ...	$C_{18}H_{32}O_2$	181·43	173·57
Linolenic acid, ...	$C_{18}H_{30}O_2$	274·10	262·15

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[1] In the case of oils absorbing large quantities of iodine, a still greater excess is preferable (about twice the quantity absorbed). In all cases the quantity of iodine used for the blank experiment should be approximately equal to the excess employed.

In actual practice, *Hübl* found that pure oleic acid took up 89·8 to 90·5 per cent. of iodine, and obtained the values quoted on p. 258 on examining a variety of fats and oils by different processes simultaneously, the substance being divided into seven classes, according to the magnitude of the iodine absorption.

Schädler gives the following values as those most generally found with various oils and fats, etc. :—

Name of Oil or Fat.	Iodine Value of	
	Oil, &c.	Fatty Acids.
Almond,	82- 83	87-90
Apricot-kernel,	100-102	...
Arachis,	94- 96	96-97
Butter,	28- 32	...
Bone,	66- 68	56-57
Cacao butter,	34	...
Castor,	93- 94	...
Charlock,	96- 97	...
Colza,	100-101	97-99
Coconut,	9- 9·5	8·5-9·0
Cotton-seed,	106-107	112-115
Curcas,	127	...
Cod-liver { medicinal,	128-130	...
Cod-liver { brown,	135-140	...
Hemp,	143-144	122-124
Hedge radish,	105	...
Japan wax,	4·2	...
Linseed,	177·178[1]	155[1]
Lallemantia (Gundschit),	162	167
Lard,	59- 60	...
Maize,	119·5	125
Nut (walnut),	142-143	...
Olive (salad),	82- 83	87-88
,, -kernel,	82	...
Palm,	51·5	...
,, -kernel,	13·5- 14	12
Poppy,	134-135	...
Pumpkin-seed,	121	...
Rape-seed,	98-100	97-99
Suet (ox tallow, beef tallow),	38- 40	26-30
Seal,	125-130	...
Sesamé,	103-105	110-111
Sunflower,	129	133-134
Sperm,	88	...
Spermaceti,	108	...
Tacamahac,	63	...
Tallow (sheep),	43-44	...
Ungnadia,	81·5-82	86-87
Wool-grease,	36	...

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[1] More recent values for linseed oil are considerably higher, probably on account of an insufficient excess of iodine or an insufficient time for complete absorption having been allowed.

The following tables represent the collected results published by numerous observers,[1] as the amounts of iodine taken up by 100 parts of different oils and fats :—

Vegetable Oils.

Name.	Minimum.	Maximum.	Average.
Fresh linseed oil, ...	170	181	175
Commercial linseed oil, . . .	148	181	170
Lallemantia oil, ...	...	...	162
Hemp-seed oil, ...	142	158	150
Nut oil, ...	143	152	146
Poppy-seed oil, ...	134	142	138
Sunflower-seed oil, ...	122	133	128
Curcas oil, ...	...	...	127
Pumpkin-seed oil, ...	...	...	121
Maize oil, ...	...	...	120
Cotton-seed oil, ...	102	111	108
Sesamé oil, ...	103	112	108
Hedge-radish oil, ...	...	...	105
Rape-seed oil, ...	99	105	101
Apricot-kernel oil, ...	99	102	100
Almond oil, ...	96	102	98
Arachis oil, ...	87·3	103	96
Mustard oil, ...	...	..	96
Castor oil, ...	83	85	84·5
Olive oil, ...	81	84·5	82·8
Olive-kernel oil, ...	...	...	81·8

Animal Oils.

Name.	Minimum.	Maximum.	Average.
Cod-liver oil, ...	126	153	140
Seal oil, ...	127	128	127
Japanese cod-liver oil, . . .	...	...	120
Bottlenose oil, ...	...	...	99·5
Porpoise oil, ...	...	...	76·8
Neat's foot oil, ...	...	...	70·3
Bone oil, ...	66	70	68
Porpoise oil oleine, ...	30·9	49·6	40·2
Bottlenose oleine, ...	...	...	32·8

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[1] Hübl, Moore, Dieterich, Wilson, Erban, Herz, Spüller, Horn, Richter, Kremel, Beringer, and Benedikt; collated by Benedikt.—*Analyse der Fette und Wachsarten*, 2nd edition, 298 and 317.

	Name of Oil.	Percentage of Iodine absorbed.	Fatty Acids.		Potassium Hydroxide. KOH, required to saponify 1000 parts of Oil.	Solution of Oil in an Equal Amount of Glacial Acetic Acid (sp. gr. 1·0562) becomes turbid at
			Melt at	Solidify at		
			° C.	° C.		° C.
I. DRYING OILS.	Linseed oil,	156-160, mean = 158	17·0	13·3	194·3	...
II. DRYING OILS.	Hemp-seed oil,	... ,, 143	19·0	15·0	193·1	...
	Nut oil,	142-144 ,, 143	20·0	16·0	196·0	...
	Poppy oil,	135-137, ,, 136	20·5	16·5	194·6	...
	Pumpkin-seed oil,	... ,, 121	28·0	24·5	189·5	108
III. MODERATELY DRYING OILS.	Sesamé oil,	105-108, ,, 106	26·0	22·3	190·0	107
	Cotton-seed oil,	105-108, ,, 106	27·7	30·5	195·0	110
	Arachis oil,	101-105, ,, 103	27·7	23·8	191·3	112
	Rape-seed oil,	97-105, ,, 100	20·1	12·2	177·0	Insoluble.
IV. NON-DRYING OILS.	Apricot-kernel oil,	99-102, ,, 100	4·5	0	192·9	114
	Almond oil,	97·5-98·9, ,, 98·4	14·0	5·0	195·4	110
	Castor oil,	84·0-84·7, ,, 84·4	13·0	3·0	181·0	Soluble in the cold.
	Olive oil,	81·6-84·5, ,, 82·8	26·0	21·2	191·7	85-111
	Olive-kernel oil,	... ,, 81·8	...	...	188·5	Soluble in the cold.
V.	Bone oil,	66·0-70·0, ,, 68·0	30·0	28·0	...	...
	Hog's lard,	57·6-60·0, ,, 59·0	...	...	195·9	...
	Artificial butter,	... ,, 55·3	42·0	39·8	...	...
VI.	Palm oil,	50·4-52·4, ,, 51·5	47·8	42·7	202·2	23
	Laurel oil,	... ,, 49·0	27·0	22·0	...	26·5
	Tallow,	... ,, 40·0	45·0	43·0	196·5	95
	Fat from suet,	... ,, 36·0	41·8	40·0	170·0	...
	Cacao butter,	... ,, 34·0	52·0	51·0	...	105
	Nutmeg butter,	... ,, 31·0	42·5	40·0	...	27
	Butter fat,	26·0-35·1, ,, 31·0	38·0	35·8	227·0	...
VII.	Coconut oil,	... ,, 8·9	24·6	20·4	261·3	40
	Japan wax,	... ,, 4·2	...	...	222·2	...

Solid Fats.

Name.	Minimum.	Maximum.	Average.
Cotton-seed "stearine,"	...	...	89·6
Goose grease,	...	...	71·5
Hog's lard,	56	63	59
Macassar oil,	...	...	53
Bone grease,	46·3	55·5	52
Palm butter,	50·3	53·9	51
Oleomargarine,	47·5	55·3	50
Laurel butter,	...	...	49
Ox tallow,	40	44	42
Sheep's tallow,	32·7	46·2	42
Wool-grease,	...	...	36
Cacao butter,	34	37·7	36
Nutmeg butter,	...	...	31
Butter fat,	19·5	38·0	30
Palm-kernel butter,	10·3	17·5	14
Coconut oil,	7·9	9·4	9
Japan wax,	...	...	4·2

Higher values still for some of the drying oils were obtained by *Holde* in the course of an investigation on the sources of error in the Hübl test,[1] the cause being assigned to more complete saturation with iodine through use of a larger excess of solution. Thus—

Linseed oil,	179-180
Hemp-seed oil,	175
Poppy-seed oil,	139-143
Sesamé oil,	106-109
Cotton-seed oil,	110-115
Common rape oil,	100-108
Refined rape oil,	100-107

The following values have also been recorded for the mixed fatty acids from various commercial oils :—

	Morawski and Demski.	Williams.
Linseed oil acids,	155·2-155·9	178·5
Hemp-seed oil acids,	122·2-125·2	...
Cotton-seed oil acids,	110·9-111·2	115·7
Sesamé oil acids,	108·9-111·4	...
Rape-seed oil acids,	96·3- 99·02	105·6
Arachis oil acids,	95·5- 96·9	...
Castor oil acids,	86·6- 88·3	93·9
Olive oil acids,	86·1	90·2

For still more recent results see the tables of Constants of the different oils in Chap. xv.

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[1] *J. Soc. Chem. Ind.*, 1891, x., 954; from *Mitth. königl. tech. Versuchsanst.*, Berlin, 1891, ix., 81.

Owing to the tendency towards absorption of oxygen exhibited by drying oils and the fatty acids obtained from them, there is always a liability to obtain somewhat different results with free fatty acids as compared with the original oils from which they were obtained, owing to partial oxidation during isolation and drying. As a rule, absorption of oxygen seems to diminish the iodine absorption as might, *a priori*, be expected.

Neglecting this alteration, the amounts of iodine absorbed by an oil, etc., and by the fatty acids isolated from it, necessarily stand to one another in the inverse ratio of their respective mean equivalent weights. For if E be the saponification equivalent of an oil, and F the mean equivalent weight of the fatty acids which it contains, quantities of oil and free acid in the respective proportion of E to F will combine with the same quantity of iodine; so that the iodine taken up by 100 parts of oil will be $\frac{F}{E}$ times that taken up by 100 parts of fatty acids—*i.e.*, if I be the iodine value of the oil and I′ that of the fatty acids—

$$I = \frac{F}{E} I'$$

and

$$I' = \frac{E}{F} I.$$

If the oil, etc., consist wholly of triglycerides, $E = F + 12{\cdot}67$; whence

$$I' = \frac{F + 12{\cdot}67}{F} I$$
$$= I\left(1 + \frac{12{\cdot}67}{F}\right).$$

Hence for fatty acids of molecular weight between 250 and 330, the iodine value of the fatty acids is between 5·1 and 3·8 per cent. greater than that of the original oil; so that for the great majority of natural oils and fats, the iodine value of the free fatty acids *exceeds* that of the oil by an amount approximating to 4·5 per cent. of the latter value.

Obviously, in some of the cases tabulated above, there must have been a considerable difference between the samples used for the determination of the iodine value of a given oil, and of that of the fatty acids derived from the same kind of oil, since the latter values are, in some instances, *less* than the former ones instead of exceeding them by about 4·5 per cent. of their value; or else considerable oxidation of the fatty acids must have taken place.

The theoretical amount of iodine corresponding with 100 parts of pure olein is 86·2 parts. From the numbers tabulated above, it is obvious that many of the fluid vegetable oils, usually regarded as non-drying (arachis, almond, apricot-kernel, etc.), contain some small amount of glycerides of the linolic or drying class, since their iodine absorptions exceed 86·2; *a fortiori*, with oils of the intermediate class exhibiting a slight amount of drying quality (cotton-seed, sesamé, sunflower, etc.), a larger iodine absorption is observed, corresponding with a still more marked proportion of drying oil constituents.

Theory of the Hübl Process.—In this case, the product formed is not simply an iodine addition product; the mercuric chloride appears to be more or less transformed into mercuric iodide, with formation of chloride of iodine, so that the addition product contains both chlorine and iodine. Thus *Hübl* concluded that oleic acid, $C_{18}H_{34}O_2$, treated with this reagent was to a large extent converted into chloriodostearic acid, $C_{18}H_{34}CHO_2$, and similarly in other cases, The chlorine thus added on is in practice never reckoned as such, but as its equivalent in iodine; so that 282 parts of oleic acid, when treated with Hübl's reagent, are regarded as combining with 2 × 127 = 254 parts of iodine, although usually the compound produced is formed by taking up 127 parts of iodine + 35·5 parts of chlorine.

Ephraim[1] came to the conclusion that iodine monochloride was formed on mixing the two portions of Hübl's solution, as represented by the equation—

$$HgCl_2 + I_2 = HgClI + ICl.$$

He prepared a solution containing 16·25 grammes of iodine chloride per litre, and with this obtained results in close agreement with the Hübl figures.

When the iodine chloride solution was titrated without previous addition of potassium iodine solution, a new value which Ephraim termed the "chlor-iodine value" was obtained. The reaction on titration was—

$$ICl + 2Na_2S_2O_3 = NaI + NaCl + Na_2S_4O_6.$$

The following chlor-iodine values were obtained:—Arachis oil, 56·6; linseed oil, 77·0; sesamé oil, 65·3; rape-seed oil, 50·4; poppy oil, 43·4; castor oil, 44·24.

Concordant results were also obtained with a solution of iodine bromide (20 grammes per litre).

Wijs[2] concludes that the following reactions occur in the absorption of halogen by oleic acid:—

$$CO_2H . C_{17}H_{33} + HIO = CO_2H . C_{17}H_{33}IOH.$$
$$CO_2H . C_{17}H_{33}I . OH + HCl = CO_2H . C_{17}H_{33}ICl + H_2O.$$

And in a part of the fat

$$CO_2H . C_{17}H_{33}ICl = CO_2H . C_{17}H_{33}I + HCl.$$

Lewkowitsch[3] does not agree with Wijs' assumption that HIO is the active agent in the absorption, which he regards as a somewhat artificial explanation not borne out by experiment. He considers that for all practical purposes it is sufficient to assume that ICl is added on to each pair of doubly-linked carbon atoms.

Wijs[4] finds that in the Hübl process the absorption takes place very rapidly at first, but more slowly afterwards.

He also points out that the time at which the blank experiment is

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[1] *Zeit. angew. Chem.*, 1895, 254.

[2] *Ibid.*, 1898, 291.

[3] *Analyst*, 1899, xxiv., 257.

[4] *Chem. Rev. Fett Ind.*, 1899, vi., 5.

titrated has also a considerable influence, as is shown by the following results obtained with a freshly-prepared solution :—

Time of Absorption.	Arachis Oil.		Linseed Oil.	
	Blank Determination.		Blank Determination.	
	Before Absorption.	After Absorption.	Before Absorption.	After Absorption.
2 hours,	87·02	...	173·74	...
7 ,,	88·23	85·38	177·65	170·39
24 ,,	90·21	82·32	181·89	163·16

In Wijs' opinion, the results obtained by titrating the blank before the absorption are probably the more correct. As regards the time of absorption, Wijs prefers seven hours, since he finds that the rapidity with which the iodine disappears reaches its lowest limit after that time.

Welmans[1] has obtained good results with a solution of 30 grammes of iodine and 30 grammes of mercuric chloride in 500 c.c. of glacial acetic acid, and made up to a litre with acetic acid. As this solution is a good solvent for fats, the use of chloroform is unnecessary.

Waller's Method.—To prevent the diminution in the amount of free iodine in Hübl's solution on standing, *Waller*[2] saturates the iodine solution with hydrochloric acid. 25 grammes of iodine are dissolved in 250 c.c. of alcohol (95 per cent.), and the solution mixed with a solution of 25 grammes of mercuric chloride in 200 c.c. of alcohol, and 25 grammes of hydrochloric acid (sp. gr. 1·19), and the liquid diluted with alcohol to 500 c.c. In a solution thus prepared, the iodine shown on titration had only fallen from 49·31 to 46·60 grammes after sixty-four days, whilst the free acid had increased to a corresponding extent.

In Waller's opinion, Hübl's iodine value represents the equivalent in iodine of the chloride, iodine, and oxygen absorbed by the fat.

His theory of the process is that the mercuric chloride is converted into free chlorine and iodide. The absorption of this chlorine by the fat is prevented by the water in the alcohol, which reacts with the chlorine, forming hydrochloric acid and oxygen. The latter combines to some extent with the fat, and prevents any further absorption of halogen.

Wijs[3] considers it probable that the absorption is not quite complete even after forty-eight hours, since Waller's solution gives lower results than the Hübl process.

In his opinion, since hydrochloric acid is not separated off from the addition compound, as in Hübl's method, the hypoiodous acid remains practically constant throughout, and therefore, the iodine value obtained when the blank is titrated after the absorption is probably the more correct, although the difference is small.

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[1] *J. Soc. Chem. Ind.*, 1900, xix., 694.

[2] *Analyst*, 1895, xx., 280.

[3] *Chem. Rev. Fett Ind.*, 1899, vi., 5.

Schweitzer and *Lungwitz*[1] describe experiments to show that a certain amount of substitution of iodine occurs in the Hübl process. They determine this amount of substitution by a method based on the reaction :—

$$5\,KI + KIO_3 + 6\,HCl = 6\,I + 6\,KCl + 3\,H_2O.$$

After titrating the free iodine in Hübl's process in the usual way, 5 c.c. of a 2 per cent. solution of potassium iodate are introduced, and the liberated iodine again titrated within five minutes with standard thiosulphate. The difference between the two titrations is multiplied by 2 in accordance with the equations—

$$6\,HI + KIO_3 = 5\,HI + HIO_3 + KI = 6\,I + 3\,H_2O + KI.$$

Schweitzer and *Lungwitz* give a number of results showing the amount of substituted iodine thus found in various oils.

Subsequently[2] the same chemists found that, by acting upon oils at a high temperature and under pressure with a solution of iodine in carbon bisulphide, in the presence of 0·6 to 0·7 gramme of powdered mercuric chloride, no substitution of iodine, expressed as hydriodic acid, occurred. The mixture was placed in stoppered bottles, sealed with mercuric iodide, and immersed in a water-bath at 60° to 80° C.

Wijs' Method.—*Wijs*[3] has based an exceedingly rapid method of determining the iodine value on the conclusions which he drew from his experiments. Since hypoiodous acid, which he regards as the chief agent in the absorption, is extremely unstable, he has devised a means of obtaining it under such conditions as largely prevent its decomposition. This is effected by preparing it by the action of water on iodine chloride.

$$ICl + H_2O = HCl + HIO,$$

a solvent being chosen which contains only so much water as will decompose nearly the whole of the iodine chloride, and which, at the same time, will not itself be oxidised by the hypoiodous acid. A solution of iodine chloride in glacial acetic acid fulfils these conditions.

It is prepared by dissolving 13 grammes of iodine in a litre of glacial acetic acid and introducing chlorine until the amount of thiosulphate required by the liquid is doubled. This point can be detected by the change in colour with a little practice. The solution thus prepared is fairly stable, and is used in the same way as the mixed Hübl solutions, except that the time of absorption is greatly reduced, only three to four minutes being required in the case of oils and fats with low iodine absorptions, and not more than ten minutes with linseed and other more unsaturated oils.

The method of preparation now commonly used is to dissolve 8·5 grammes of iodine and 7·8 grammes of iodine trichloride in a litre of acetic acid.

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[1] *J. Soc. Chem. Ind.*, 1895, xiv., 130.

[2] *Ibid.*, 1895, xiv., 1030.

[3] *Ber. d. d. chem. Ges.*, 1898, xxxi., 750.

The following table, by *Wijs*, shows the amount of iodine consumed by the fat in one minute by different solutions :—

	Arachis Oil.		Linseed Oil.	
	Absorbed in 1 Minute.	Per cent. of Iodine Value.	Absorbed in 1 Minute.	Per cent. of Iodine Value.
Wijs' solution, . .	86·91	98·9	174·07	98·1
Hübl's solution, 16 hours old, . .	82·54	93·9	152·46	85·9
Hübl's solution, 5 days old, . .	...	...	128·90	72·6
Waller's solution, .	73·52	83·6	102·64	57·8

Lewkowitsch[1] agreed with Wijs in concluding that both this new method and the Hübl process yielded practically identical results, provided that the older method was used with certain precautions. Thus, the Hübl solution should be allowed to stand for a day before use, the blank titration should be made before the absorption, and the solution should not be allowed to act upon the fat for more than seven hours.

Results obtained by *Williams* are given in the table illustrating the absorption of bromine by oils (*supra*).

Ponzio and *Gastaldi*[2] have shown that, whilst the iodine value of oleic acid estimated by the usual methods is in close agreement with the theoretical value, the results obtained with certain other unsaturated fatty acids, such as crotonic acid, are much too low. For example, the following results were obtained :—

Unsaturated Acid.	Hübl.	Wijs.	Hanus.	Theoretical Value.
Undecylenic acid, $CH_2 : CH(CH_2)_8 . COOH$,	135·1	137·3	..	137·8
Crotonic acid, $CH_3 . CH : CH . COOH$, .	17·4	10·3	4·3	295·0
2-3-Hypogæic acid, $CH_3(CH_2)_{12}CH : CH . COOH$, .	6·6	20·4	1·9	99·8
2-3-Oleic acid, $CH_3(CH_2)_{14} . CH : CH . COOH$, .	8·7	18·0	3·0	89·7

It thus appears that the position of the double bond in unsaturated fatty acids of the series $C_nH_{2n-2}O_2$ influences the amount of the iodine value. If the double bond is distant from the carboxyl group, as in ordinary oleic and undecylenic acids, the iodine value will be normal, whilst if it adjoins the carboxyl group the iodine value will be lower than theory requires. This influence, however, only affects the velocity of the reactions, and by prolonging the absorption to 70 hours, with Wijs' solution 2-3 oleic acid gave an iodine value of 86·8. Determination

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[1] *Analyst*, 1899, xxiv., 259.

[2] *Gazz. Chim. Ital.*, 1912, xlii., 92.

of the iodine value thus appears to be a good method of establishing the position of the double bond in an unsaturated acid.

Experiments made by *Mergen* and *Winogradoff*[1] have shown that, of the various solutions used for determining the iodine value of fats, *Waller's* is the most and *Hübl's* the least stable. In estimating the iodine value of an unknown compound, *Wijs'* method is the most trustworthy. After the titration with thiosulphate the liquid should be extracted with cold water, and the aqueous extract titrated with N/10 alkali to find the amount of halogen acid. For example, in a test experiment pure oleic acid, after treatment for 30 minutes with *Wijs'* solution, showed an iodine value of 99·95 (theory = 89·95), whilst the acid in the aqueous solution corresponded to 4·62 per cent. of substituted iodine. In a parallel determination with the same oleic acid, but with a *Wijs'* solution containing an excess of 2 per cent. of iodine over the chlorine, the iodine value was 90·95, whilst the acid in the aqueous extract corresponded to 0·53 per cent. of substituted iodine.

St. Weiser and *Donath*[2] have shown that *Winkler's* bromate method gives results in close agreement with those obtained by *Wijs'* method:—A weighed quantity of the fat is dissolved in 10 c.c. of carbon tetrachloride, 50 c.c. of N/10 potassium bromate solution, and 1·5 grammes of potassium bromide added, and the mixture acidified with 10 c.c. of 10 per cent. hydrochloric acid and left for 2 to 4 hours in a dark place. Fifteen c.c. of 10 per cent. potassium iodide solution are then added, and the liberated iodine titrated.

Iodine Bromide Solution.—*Hanus*[3] recommends the use of a solution of 10 grammes of iodine bromide in 500 c.c. of glacial acetic acid. The bromide is prepared by the interaction of 13 grammes of bromine introduced drop by drop into a flask containing 20 grammes of finely-powdered iodine, the temperature not being allowed to exceed 5° to 8° C.

From 0·1 to 0·7 gramme of the oil is dissolved in 10 c.c. of chloroform, and the solution mixed with 25 c.c. of the iodine bromide solution. After fifteen minutes 15 c.c. of a 10 per cent. solution of potassium iodide are added, and the liquid titrated with standard thiosulphate solution. The iodine bromide reagent is also standardised with thiosulphate. The results thus obtained are in close agreement with those given by Hübl's process.

V. THE ACETYL VALUE

(*Benedikt and Ulzer's Test*).

When organic substances containing alcoholiform hydroxyl are heated in contact with acetic anhydride, an action takes place which may be regarded as the converse of saponification or hydrolysis; the

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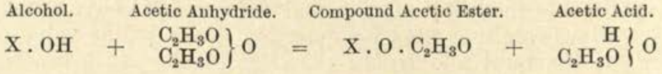
[1] *Zeit. angew. Chem.*, 1914, xxvii., 241.

[2] *Zeit. Untersuch. Nahr. Genussm.*, 1914, xxviii., 65.

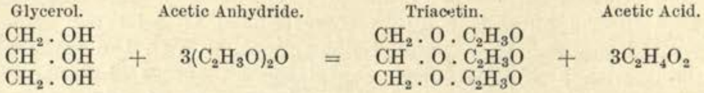
[3] *Zeit. Untersuch. Nahr. Genussm.*, 1901, iv., 913.

hydroxylated body, X . OH, acts upon the anhydride in accordance with the equation—



$$\begin{array}{ccccccc} \text{Alcohol.} & & \text{Acetic Anhydride.} & & \text{Compound Acetic Ester.} & & \text{Acetic Acid.} \\ X.OH & + & \left.\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\right\} O & = & X.O.C_2H_3O & + & \left.\begin{matrix} H \\ C_2H_3O \end{matrix}\right\} O \end{array}$$

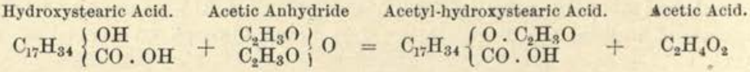
giving rise to a compound ester. Polyhydroxylated bodies behave in the same way, one acetyl group being taken up for each alcoholiform hydroxyl group present. Thus glycerol treated with acetic anhydride becomes transformed into triacetin in accordance with the equation—



$$\begin{array}{ccccccc} \text{Glycerol.} & & \text{Acetic Anhydride.} & & \text{Triacetin.} & & \text{Acetic Acid.} \\ \begin{matrix} CH_2.OH \\ CH\ .OH \\ CH_2.OH \end{matrix} & + & 3(C_2H_3O)_2O & = & \begin{matrix} CH_2.O.C_2H_3O \\ CH\ .O.C_2H_3O \\ CH_2.O.C_2H_3O \end{matrix} & + & 3C_2H_4O_2 \end{array}$$

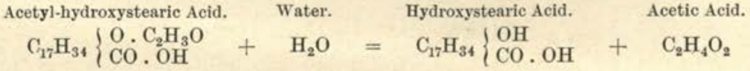
On this reaction is based a method for the analytical examination of commercial glycerol (Chap. XXII.).

Benedikt and *Ulzer* also attempted to utilise this reaction to distinguish hydroxylated organic acids (like hydroxystearic and ricinoleic acids) from non-hydroxylated acids, such as stearic and palmitic acids. Their method is based on the assumption that acetic anhydride exerts no action on the hydroxyl of the CO . OH group of an organic acid, but does act, in accordance with the above equation, on any alcoholiform hydroxyl contained therein; so that if, for example, stearic acid be treated with acetic anhydride, and the product heated with water so as to decompose excess of acetic anhydride, simply unchanged stearic acid results,[1] whereas, if hydroxystearic acid be similarly treated, *acetyl-hydroxystearic acid* is produced, thus—



$$\begin{array}{ccccccc} \text{Hydroxystearic Acid.} & & \text{Acetic Anhydride} & & \text{Acetyl-hydroxystearic Acid.} & & \text{Acetic Acid.} \\ C_{17}H_{34}\left\{\begin{matrix} OH \\ CO.OH \end{matrix}\right. & + & \left.\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\right\} O & = & C_{17}H_{34}\left\{\begin{matrix} O.C_2H_3O \\ CO.OH \end{matrix}\right. & + & C_2H_4O_2 \end{array}$$

The acetylated acids thus formed are stated to be moderately stable, not being appreciably hydrolysed by the action of the hot water required to decompose the excess of acetic anhydride present. Accordingly, if after thus removing excess of acetic anhydride, the resulting acetyl acid be titrated with standard alkali, one equivalent of alkali will be directly neutralised; whilst if it be heated with excess of alcoholic alkali so as to saponify it, reproducing hydroxystearic acid and acetic acid, thus—



$$\begin{array}{ccccccc} \text{Acetyl-hydroxystearic Acid.} & & \text{Water.} & & \text{Hydroxystearic Acid.} & & \text{Acetic Acid.} \\ C_{17}H_{34}\left\{\begin{matrix} O.C_2H_3O \\ CO.OH \end{matrix}\right. & + & H_2O & = & C_{17}H_{34}\left\{\begin{matrix} OH \\ CO.OH \end{matrix}\right. & + & C_2H_4O_2 \end{array}$$

two equivalents will be neutralised in all, the second by the acetic acid formed.

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[1] This assumption is entirely at variance with the results obtained by Lewkowitsch (*vide infra*).

In the case of a mixture of acids containing hydroxylated and non-hydroxylated constituents, the proportion of the latter can be estimated by determining the extra amount of potassium hydroxide neutralised on saponification, as compared with that neutralised directly. The term "acetyl value" (*Acetylzahl*) is used to indicate the weight of potassium hydroxide (KOH = 56·1) neutralised by the acetic acid formed from 1,000 parts of mixed acetylated product.[1]

Benedikt and Ulzer's Process.—The acetylation process, as devised by *Benedikt* and *Ulzer*, is carried out thus:—The free fatty acids formed by saponifying a given sample of oil and decomposing the soap by a mineral acid, are boiled for two hours with an equal volume of acetic anhydride in a flask under a reflux condenser. The mass is then boiled for half an hour with about 20 parts of water; the acetic acid solution formed is siphoned off, and the treatment with boiling water repeated three times, so that finally the water is free from acidity after boiling for half an hour. The acetylated product is then filtered through a dry filter paper to remove water, and a weighed quantity dissolved in pure alcohol. Standard alcoholic potassium hydroxide is added until the liquid is neutral, and the amount neutralised noted. More than as much again is then added, and the whole heated to boiling whereby the acetyl derivative is saponified, after which the unneutralised alkali is then titrated back. Thus in the case of the fatty acids from a sample of castor oil the following figures were obtained[2]:—3·379 grammes of acetylated product neutralised 17·2 c.c. of semi-normal potassium hydroxide, whence the "acetyl acid value" is 142·8. After addition of 32·8 c.c. more potassium hydroxide solution and boiling, 14·3 c.c. were found to be unneutralised, whence 18·5 c.c. represent the acetic acid formed on saponification, giving the "acetyl value" 153·6, and the "acetyl saponification value" 142·8 + 153·6 = 269·4. Since the acetyl value exceeded the acetyl acid value, it would follow that some amount of a *dihydroxylated* acid was present, especially as the mixed acids of castor oil contain a small quantity of stearic (non-hydroxylated) acid to begin with (*vide infra*).

Operating in this way, *Benedikt* and *Ulzer* obtained the following values for various oils:—[3]

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[1] *Benedikt* and *Ulzer* termed the potassium hydroxide directly neutralised by 1,000 parts of mixed acetylated product, the "acetyl acid value" (*Acetylsäurezahl*), and the total neutralised on saponification (sum of *Acetylzahl* and *Acetylsäurezahl*) "the acetyl saponification value" (*Acetylverseifungszahl*). Thus the theoretical values for acetyl-hydroxyoleic (ricinoleic) acid are—

Acetyl value, ...	165·0
Acetyl acid value, ...	165·0
Acetyl saponification value, . . .	330·0

[2] Benedikt, *Analyse der Fette und Wachsarten*, 2nd edition, 1892, 114.

[3] *Monatsh. f. Chem.*, 1887, viii., 41.

Oil Used.	"Neutralisation Value" of Fatty Acids before Acetylation.	Acetyl Acid Value.	Acetyl Value.	Acetyl Saponification Value.
Arachis, . . .	198·8	193·3	3·4	196·7
Cotton-seed, . .	199·8	195·7	16·6	212·3
Croton, . . .	201·0	195·7	8·5	204·2
Hemp-seed, . .	199·4	196·8	7·5	204·3
Linseed, . . .	201·3	196·6	8·5	205·1
Almond, . . .	201·6	196·5	5·8	202·3
Poppy-seed, . .	200·6	194·1	13·1	207·2
Nut, ...	204·8	198·0	7·6	205·6
Olive, . . .	197·1	197·3	4·7	202·0
Peach-kernel, . .	202·5	196·0	6·4	202·4
Castor, . . .	177·4	142·8	153·4	296·2
Rape, . . .	182·5	178·5	6·3	184·8
Sesamé, . . .	200·4	192·0	11·5	203·5
"Soluble castor oil,"	...	184·5	62·2	246·7

J. A. Wilson [1] found the following average values for castor, olive, and cotton-seed oils :—

	Acetyl Acid Value.	Acetyl Value.	Acetyl Saponification Value.
Castor oil, ...	136·7	155·0	291·7
Olive oil, ...	170·0	36·0	206·0
Cotton-seed oil, ...	189·5	21·0	120·5

Obviously these figures do not agree very sharply with the preceding ones. If the results of the acetyl test could have been regarded as perfectly trustworthy, these values would have indicated the existence of more or less considerable amounts of hydroxy acids in all the samples examined, amounting, in the case of the cotton-seed and sesamé oils examined by *Benedikt* and *Ulzer*, to 6 to 8 per cent. of the total acids present, and to much larger amounts in the case of the olive and cotton-seed oils examined by *Wilson*. The figures, however, do not exhibit such concordance as to be unexceptionable. The effect of acetylating the hydroxylated constituents of a mixture of acids containing only a small proportion of hydroxylated acids would be to cause the neutralisation value of the acetylated fatty acids (the acetyl acid value) to be only slightly less than their neutralisation value before acetylation, whereas the observed differences are materially larger. Thus the neutralisation numbers of oleic, hydroxyoleic, and acetyl hydroxyoleic acids are respectively 198·9, 188·25, and 165·0; whence a mixture of 90 parts oleic acid and 10 parts hydroxyoleic

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[1] *J. Soc. Chem. Ind.*, 1892, xi., 495.

acid would have the neutralisation number 197·9; and after acetylation would furnish a mixture of oleic and acetyl hydroxyoleic acids having the neutralisation number (acetyl acid value) 195·5, or only 2·4 less than the original mixture.

Similarly a mixture of 95 parts oleic acid and 5 parts hydroxyoleic acid would have the neutralisation value 198·4 before acetylation, and 197·2 after, giving the difference 1·2. The actual differences calculated from the above figures obtained by *Benedikt* and *Ulzer* with oils other than castor oil, vary between − 0·2 (olive oil) and + 8·4 (sesamé oil), but in most cases amount to 5 to 6; strongly suggesting that some cause is at work abnormally diminishing the "acetyl acid value" by some units, and, in consequence, giving an apparent "acetyl value" of some units in magnitude, the result of this cause, and not of the existence of hydroxy acids in the fatty acids examined. The same conclusion also follows from the figures obtained with castor oil acids, as the supposition that a considerable percentage of dihydroxylated acids is present is manifestly untenable.

Lewkowitsch was the first to throw light on the probable cause of these discrepancies.[1] According to his results, by the action of acetic anhydride in excess the higher acids of the acetic family (such as lauric, palmitic, and stearic acids, etc.) become more or less completely converted into the corresponding anhydrides.[2] When the products freed from the excess of acetic anhydride by the action of water are neutralised by alkali, a diminution in the apparent amount of free acid is noticed proportionate to the amount of fatty anhydrides present not decomposed by the water treatment; and when the neutralised substance is heated with excess of alcoholic alkali, and subsequently titrated back, a quantity of alkali is neutralised proportionate to the fatty acid formed by the hydration of the fatty acid present; so that an apparent "acetyl value" is obtained even when no alcoholiform hydroxyl whatever is present in the body examined. Thus he obtained the figures in table, p. 270, with samples of capric, lauric, palmitic, oleic, stearic, and cerotic acids in a state of only approximate purity so far as chemical identity is concerned, but at any rate free from any notable amount of hydroxy acids.

From these figures it obviously results that but little reliance is to be placed on the result of the acetylation test for alcoholiform hydroxyl in fatty acids when based simply on the titration process above described. Good results, however, can be obtained by *Lewkowitsch's*[3] modification of the test, in which the acetylated product is saponified with alcoholic potassium hydroxide, the alcohol boiled off, and the residue distilled with dilute sulphuric acid, much as in Reichert's test

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[1] *Proc. Chem. Soc.*, 1890, 72 and 91.

[2] Anschütz found (*Ann. Chem. Pharm.*, 1884, ccxxvi., 6) that when acetic anhydride and benzoic acid were heated together in a sealed tube at 220° C. benzoic anhydride was produced; whilst the dibasic acids, succinic, camphoric, orthophthalic, and diphenic acids were largely transformed into their respective anhydrides by being heated with acetic anhydride at 120° to 150° C.

[3] *J. Soc. Chem. Ind.*, 1890, ix., 842.

Fatty Acid Used.	Neutralisation Value.		Acetyl Acid Value.	Acetyl Value	Acetyl Saponification Value.
	Theoretical Value for Pure Fatty Acid.	Found.			
Capric, . .	326·2	318 05	176·40	174·00	350·40
Lauric, . .	280·5	273·02	161·50	132·49	293·99
Palmitic, . .	219·1	213·4	143·53	82·60	222·13
Oleic, . . .	198·0	183 0	116·50	125·55	242·05
Stearic, . .	197·5	203 0	138·89	82·29	221·18
Cerotic, . .	136·8	128·4	73·87	68·23	142·10

(*vide infra*). Any acetic acid formed by hydrolysis of acetyl derivatives is thus distilled over, and may be titrated by means of standard alkali.

In this way dihydroxystearic acid (from oleic acid) was found to form the anhydride of diacetylhydroxystearic acid—

$$\left.\begin{matrix} C_{17}H_{34}\,(O\,.\,C_2H_3O_2\,.\,CO \\ C_{17}H_{34}\,(O\,.\,C_2H_3O_2\,.\,CO \end{matrix}\right\}O,$$

on treatment with acetic anhydride. The amount of acetic acid obtained from this on saponification and distillation was but little below the theoretical quantity.

On the other hand, the old acetylation test gives good results with bodies not of an acid character, containing alcoholiform hydroxyl, more especially in the case of the higher homologues of ethylic alcohol. Thus in the examination of waxes and bodies generally that give rise to higher alcohols, the amount of hydroxylated substances present may be measured by converting them into compound esters by means of acetic anhydride, and determining the amount of potassium hydroxide neutralised on saponifying the product. Pure cetylic alcohol, $C_{16}H_{33}\,.\,OH$, for instance, furnishes an acetyl derivative, *cetyl acetate*, $C_{16}H_{33}\,.\,O\,.\,C_2H_3O$, of molecular weight 284—*i.e.*, 984 milligrammes of cetyl acetate will furnish 60 milligrammes of acetic acid on saponification, neutralising 1 c.c. of normal potassium hydroxide solution containing 56·1 milligrammes of potassium hydroxide (KOH); whence the "acetyl value" of cetyl acetate is $\frac{56{\cdot}1}{284} \times 1{,}000 = 197{\cdot}5$.

If a given sample of cetylic alcohol (known to contain foreign matter not capable of forming acetyl derivatives) furnish an acetyl derivative of which the acetyl value is found to be 98, obviously about one-half of the substance is cetylic alcohol. A more exact value is obtained by determining the quantity of foreign matter present, subtracting that from the weight of acetylated product, and reckoning the acetyl value on the difference as 1,000, in a way similar to that adopted in the parallel case of the determination of the saponification value of a saponifiable body after correction for unsaponifiable matters present.

In the case of impure glycerol the acetylation test is employed in a similar way; 92 parts of pure glycerol would furnish $3 \times 60 = 180$ parts of acetic acid on saponification of the triacetin formed therefrom, and this acid would neutralise $3 \times 56{\cdot}1 = 168{\cdot}3$ parts of potassium hydroxide. If a given sample of impure glycerol were found to neutralise n parts of potassium hydroxide per 92 of substance, the percentage of glycerol present would be $\frac{n}{168{\cdot}3} \times 100$. Or otherwise, 92 milligrammes of pure glycerol would furnish acid neutralising 3 c.c. of normal alkali solution; hence if a weight, w milligrammes, of impure glycerol furnish acid neutralising x c.c. the percentage of glycerol would be $\frac{\frac{x}{3} \times 92}{w} \times 100 = \frac{x}{w} \times 3{,}066{\cdot}7$.

In the examination of the unsaponifiable matters left on treating oils and fats, etc., with alkalis, the substance may conveniently be converted into acetyl derivatives by treatment with acetic anhydride, boiled with water to decompose excess of anhydride, crystallised from alcohol, and examined as to the acetyl value obtained on saponification of the product. Thus, cholesteryl acetate ($C_{26}H_{43} . O . C_2H_3O$) and its isomerides give the number 135·5.

Lewkowitsch,[1] in an admirable experimental study, has shown that the acetyl value is an indication of—(1) hydroxy acids; (2) free alcohols; (3) oxidised fatty acids; (4) acids of unknown constitution; (5) mono- and diglycerides; and (6) rancidity.

By determining the acetyl values of both the glycerides and free fatty acids (avoiding oxidation) it is possible to obtain information as to the nature of the glycerides. If the two values are identical the inference is that only triglycerides are present.

Lewkowitsch's Method.—In carrying out the process devised by *Lewkowitsch*,[2] referred to above, 10 grammes of the filtered fat are boiled for two hours with an equal volume of acetic anhydride under a reflux condenser, and the product boiled with several hundred c.c. of water in a large beaker, bumping being prevented by the introduction of a slow current of carbon dioxide through a fine tube reaching nearly to the bottom. The boiling is continued for thirty minutes, after which the aqueous layer is withdrawn and the oil boiled twice more with the same quantity of water for the same time.

The acetylated substance is next freed from water, and filtered. About 5 grammes are then saponified with a definite quantity of standard alcoholic potassium hydroxide, the alcohol evaporated off, and the soap dissolved in boiling water.

The amount of acetate present is then determined by either a *distillation* or *filtration process*.

In the former an excess of dilute sulphuric acid (1 : 10) is introduced, from 500 to 700 c.c. of the liquid distilled, by blowing a current

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[1] *Analyst*, 1899, xxiv., 319.

[2] *J. Soc. Chem. Ind.*, 1897, xvi., 509; and *Analyst*, 1899, xxiv., 319.

of steam through the flask, and the distillate filtered and titrated with deci-normal alkali, as in the determination of the Reichert value.

In the filtration process, which is the more rapid, an amount of sulphuric acid exactly equivalent to the alcoholic alkali used, is added, the liquid heated, the layer of fatty acid filtered off, and washed with boiling water, and the filtrate and washings titrated with the standard alkali.

Free alcohols (cholesterol, etc.) will also be saponified, and, if present in any quantity, a correction must be made for them. It is also necessary to make a deduction for the amount of alkali neutralised by the volatile fatty acids present.

A selection from the results published by *Lewkowitsch*[1] is given in the subjoined table :—

Oil or Fat.	I.	II.	III.
	Total Volatile Acids = Mgrms. of KOH per grm.	Apparent Acetyl Value.	True Acetyl Value. II.-I.
Linseed, I., . . .	2·9	6·85- 6·92	3·98
,, III., . . .	0·8	12·5	...
Maize, ...	2·53	8·21- 8·75	5·81
Curcas,.	...	7·5	...
Castor, I., ...	0·0	149·6 -150·5	150·05
,, II., ...	0·0	149·4 -149·9	149·65
Colza, ...	2·15	16·6 - 17·2	14·75
Olive, ...	2·54	12·78- 13·48	10·64
Horse's foot, . . .	4·08	12 96- 14·40	9·44
Animal, ...	3·73	22·04- 22·38	18·48
Fish, ...	9·22	41·88	32·66
Japan fish, ...	1·78	13·3 - 13·5	11·77
Seal, ...	1·50	16·47- 16·84	15·18
Cod-liver (old), . . .	2·60	7·9 - 8·9	5·8
,, (fresh), . . .	3·60	4·75	1·15
Skate-liver, ...	0·80	10·60- 11·20	10·1
Shark-liver, ...	2·95	11·88- 11·95	8·97
Cotton-seed, I., . . .	6·28	24·76- 25·1	15 65
,, V., . . .	0·99	15·8	14·8
Palm (23·8 per cent. free fatty acids), . . .	2·34	17·8 - 18·8	15·96
Sawarri, ...	1·07	6·47- 8·9	6·61
Cacao butter, . . .	...	2·71- 2·86	...
Japan wax, I., . . .	10·05	27·3	17·25
,, II., . . .	5·6	31·2 - 33·1	26·55
Lard, ...	6·6 - 6·7	9·3	2·65
Bone fat (42·6 per cent. free fatty acids), . . .	4·22	15·54- 15·59	11·34
Tallow, ...	1·3	9·4 - 10·4	8·6
Croton, ...	21·07-21·09	40·68- 41·09	19·82
Palm-nut.	11·4	19·0	7·6
Coconut, I., . . .	20·9	23·2	2·3
,, II., . . .	21·9	28·8	6·9
Butter fat, I., . . .	49·3 -49·4	48·48- 49·29	9·45
,, II., . . .	43·32	45·23	1·91
,, IV., . . .	32·0	39·4 - 41·0	8·55

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[1] *Analyst*, 1899, xxiv., 319.

Holland[1] suggests that, in order to be really comparable with other values in fat analysis, the acetyl value should indicate the number of milligrammes of potassium hydroxide required to saponify the acetyl taken up by 1 gramme of fat on acetylation. A rapid method of determining the value is adapted from various processes, as follows :—Five grammes of the fat are heated with 10 c.c. of acetic anhydride on a water-bath beneath a reflux condenser, and after 1 to 1½ hours sufficient ceresin is added to form a solid disc when cold. Prior to cooling, 150 c.c. of boiling water are introduced, and the flask heated on the water-bath, with occasional shaking, to remove occluded acetic acid. The solid cake, left on cooling, is heated with more boiling water until a nearly neutral filtrate is obtained. The solid disc and particles on the filter are boiled with 50 c.c. of standard alcoholic potassium hydroxide solution and 50 c.c. of alcohol beneath a reflux condenser, and the excess of alkali titrated with standard hydrochloric acid. The difference between the saponification values before and after acetylation is the acetyl value.

VI. METHYL IODIDE TEST—ZEISEL'S TEST.

Compound esters of methylic alcohol and its next higher homologues do not appear to have been hitherto recognised as important constituents of natural fixed oils and fats, although the corresponding compounds of the higher homologues of methylic alcohol, such as cetylic alcohol, are well marked constituents of certain cetacean oils, waxes, etc. Many essential oils, however, contain constituents of analogous character—*e.g.*, oil of wintergreen, largely consisting of *methyl salicylate*, $C_6H_4\left\{\begin{array}{l}OH\\CO\,.\,O\,.\,CH_3\end{array}\right.$. Another class of essential oils containing the methoxyl group ($O\,.\,CH_3$) also exists, in which the hydrogen displaced by methyl is alcoholiform in character, and not contained in the organic acid group $CO\,.\,OH$. Thus, *anethol* or anise oil camphor is the methylic ester of a phenoloid derived from allylbenzene, $C_3H_5\,.\,C_6H_4\,.\,O\,.\,CH_3$.

When substances containing a methoxyl group are heated in contact with hydriodic acid, a reaction is brought about whereby the methyl group is eliminated in the form of *methyl iodide*, thus—

$$\overset{\text{Methoxyl Compound.}}{X\,.\,O\,.\,CH_3} \quad + \quad \overset{\text{Hydriodic Acid.}}{HI} \quad = \quad \overset{\text{Methyl Iodide.}}{CH_3I} \quad + \quad \overset{\text{Hydroxyl Compound.}}{X\,.\,OH}$$

A test for the presence of methoxyl in certain bodies (*e.g.*, codeine) based on this action was employed by the author (A. W.) as far back as 1871[2], the methyl iodide vapours evolved being passed through a red hot combustion tube containing lead chromate, so as to burn the methyl iodide, the resulting carbon dioxide being absorbed by potash bulbs in the usual way. *Zeisel*[3] modified the process by determining the

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[1] *J. Ind. Eng. Chem.*, 1914, vi., 482.

[2] *Proc. Royal Soc.*, 1871, xx., 8.

[3] *J. Soc. Chem. Ind.*, 1886, v., 335; from *Monatsh. f. Chem.*, vi., 989. See also *J. Soc. Chem. Ind.*, 1889, viii., 735 and 925 (*Benedikt* and *Grüssner*).

iodine contained in the methyl iodide produced instead of the carbon. For this purpose the vapours of methyl iodide evolved are carried off by a stream of carbon dioxide and received in bulb tubes containing alcoholic silver nitrate, intercepting vessels, etc., being employed to prevent vapours of hydriodic acid or iodine from also passing over. On standing, diluting with water, and adding nitric acid, silver iodide is precipitated, the weight of which is a measure of the amount of methyl iodide formed, and consequently of the proportion of methoxyl-containing substances present.

Fig. 40 represents the arrangement employed by *Benedikt* and *Grüssner*. A few decigrammes of substance are heated with 10 c.c. of hydriodic acid solution of specific gravity 1·70 in the flask A, warmed by means of a glycerol bath. A current of carbon dioxide is led through the flask, the issuing vapours passing through a 3-bulb condenser, bulb I. being empty to condense steam, etc.; bulb II. containing water to absorb hydriodic acid; and III., red phosphorus and water to retain any traces of free iodine evolved by decomposition of hydriodic acid by heat. After passing through the bulbs the carbon dioxide, mixed with methyl iodide vapour, is led into the flask B containing 5 c.c. of

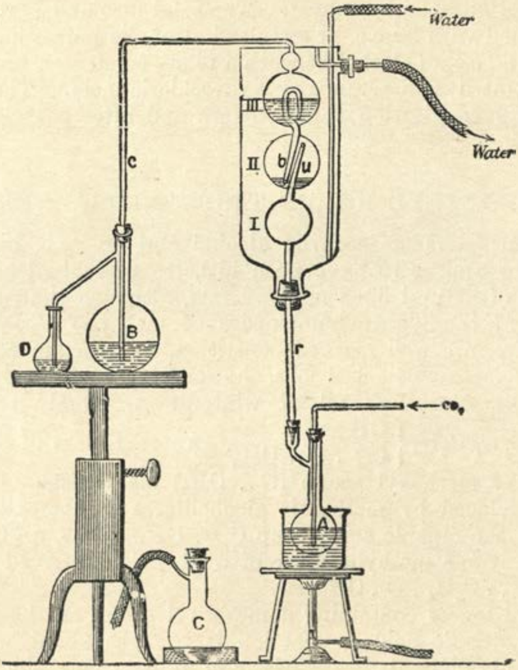

Fig. 40.—Benedikt and Grüssner's Apparatus for Zeisel's Test.

a 40 per cent. solution of silver nitrate and 50 c.c. of 95 per cent. alcohol; the safety flask D contains 1 c.c. of the same silver solution with 10 c.c. of alcohol, but is usually unnecessary, all methyl iodide being retained in the first flask B.

Substances containing ethoxyl ($O . C_2H_5$) and homologues are similarly affected; as the molecular weight of the alkyl iodide formed increases, slight differences in manipulation become necessary, principally consisting in the employment of a higher temperature to enable the alkyl iodide vapours to pass over; for which reason the method is only applicable to the lower members of the series and not to compound esters of the higher alcohols, such as cetylic alcohol.

The term "methyl value" is conveniently employed to indicate the weight of methyl ($CH_3 = 15$) equivalent to the silver iodide thus formed from 1,000 parts by weight of substance. If a weight, w milligrammes, of substance give n milligrammes of silver iodide (equivalent to $n \times \frac{15}{235}$ milligrammes of CH_2) the methyl value, M, is obviously given by the equation—

$$\begin{aligned} M &= \frac{n}{w} \times \frac{15{,}000}{235} \\ &= \frac{n}{w} \times 63{\cdot}83. \end{aligned}$$

Thus, 296·3 milligrammes of oil of cloves gave 373·7 milligrammes of silver iodide, whence $M = \frac{373{\cdot}7}{296{\cdot}3} \times 63{\cdot}83 = 80{\cdot}5$. The theoretical methyl value for pure *eugenol*, $C_{10}H_{12}O_2$, or $C_3H_5 . C_6H_3 \left\{ \begin{matrix} OH \\ O . CH_3 \end{matrix} \right.$ is 91·5; whence the sample examined contained $\frac{80{\cdot}5}{91{\cdot}5} = 87{\cdot}9$ per cent. of eugenol. Similarly, a sample of anise oil gave the methyl value 82·8; since pure *anethol*, $C_3H_5 . C_6H_4 . O . CH_3$, corresponds with the methyl value 101·4, the sample contained $\frac{82{\cdot}8}{101{\cdot}4} = 81{\cdot}6$ per cent. of anethol.

Relationship between the Constants of Fats.—It has often been noticed that a certain relationship exists between some of the chemical and physical values of fats, such as, for example, the refractive index and the iodine value. This relationship has recently been shown by Backer[1] to hold good for the principal constants—viz., the refractive index, n, specific gravity, d, saponification value, V, and iodine value, I., of ordinary fats, and it may be expressed by the equation—

$$\frac{n^2t - 1}{n^2t + 2} \times \frac{100}{d\frac{t}{4}} = 33{\cdot}07 + 0{\cdot}00075\,I - 0{\cdot}01375\,V + 0{\cdot}002\,(t - 15).$$

In the presence of hydroxy acids the first figure of the equation is lower.

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[1] *Chem. Weekblad*, 1916, xxxv., 954.

§ 4. Processes Used for Extracting, Rendering, Refining, and Bleaching Oils, Fats, &c.

CHAPTER IX.

EXTRACTION OF OILS FROM SEEDS, ETC., BY PRESSURE OR SOLVENTS.

EARLIER FORMS OF PRESS.

The use of olives and various kinds of seeds and nuts as sources of oil has been known from at least the commencement of the historic period, the earliest appliances for the expression of the fluid consisting of "mills" somewhat after the fashion of the primeval corn grinding hand mills, in which a rounded stone was made to revolve in a basin-shaped stone vessel by means of projecting handles, worked usually by two women seated on the ground on opposite sides of the mill.[1] The pulp thus produced was then placed in sacking and pressed by means of planks weighted with stones, very much as grape juice was expressed in the earlier form of wine press; or a powerful lever was applied, somewhat after the style of an enormous lemon squeezer.

Various forms of lever press have been in use at different times, some of more complex order than the simple lemon squeezer type of machine, a bent lever working a cam pressing upon the upper board so as to force it downwards; or the pressure board being arranged vertically, and the sacking being compressed between it and a stout vertical standard, such as the stump of a tree. Double action presses of this kind, working alternately, have also been constructed. A further improvement in oil-pressing appliances was the introduction of wedges between the pressure boards, actuated by levers and cams or by percussion; in the latter case, the press consisted of a stout frame-work of beams, inside of which the pressure boards and seed bags were arranged, so that by hammering in wedges between adjacent pairs of boards, or between the boards and the frame-work, the seed bags were gradually compressed and finally subjected to considerable pressure. Even at the present day lever presses and wedge presses

[1] "There shall be two women grinding together; the one shall be taken, and the other shall be left."—Luke xvii. 35.

of a more or less rude manufacture, but of considerable practical efficiency, are still in use to a considerable extent among those nations and in those districts to which improved machinery and engineering appliances have not yet penetrated—*e.g.*, in China and some parts of Japan[1]—whilst improved modifications of the older lever press, constructed with elbow levers actuated by steam or water power, are employed with advantage for various oil and grease expression purposes (*vide infra*).

Screw presses have also been extensively used, and are still largely employed in the smaller factories; but of late years they have been, for the most part, superseded by hydraulic presses in the larger and more modern seed oil mills. In similar fashion various forms of appliances have been successively introduced and used for the crushing of oil-containing material, and otherwise treating it previously to expression, so as to render the flow of oil more easy and complete. Thus pairs of crushing rollers working on parallel axes so as to squeeze the olives, seeds, etc., introduced between them, and "edge-runners" (Fig. 55) arranged like a mortar-mill, are more recent developments which have, for the most part, superseded the older form of "stamps" in which mechanically worked pestles pounded the seed, etc., in large basins or mortars.

Even at the present day a considerable amount of oil of various kinds is manufactured (on the small scale) by a process probably of greater antiquity still than any mechanical expression method. In most tropical and subtropical countries oleiferous seeds and nuts of various kinds abound. In order to extract the oil these are simply pounded or crushed and then boiled with water, the oil rising to the top and being skimmed off. Experience has generally guided the natives to the use of a previous *roasting* of the nuts or beans, the effect of the heat being to coagulate and solidify mucilaginous and albuminous matter, rendering the after separation of the oil by means of water much more easy and complete. Castor oil, for example, is thus largely extracted for local use in India; whilst palm oil and palm-nut oil, until comparatively recently, were almost wholly prepared by this method, all the oil shipped from Africa having been extracted by a water-boiling process applied to the pulp and roasted kernels. Of late years, however, it has been more usual to separate the kernels from the pulp and export them untreated, the oil being subsequently extracted by the ordinary expression or solvent processes.

In the rural olive-producing districts a considerable amount of oil is prepared by a sort of combination of the two methods, the appliances being somewhat rude and primeval in the smaller oil factories, but more modern in the larger ones. The crushed pulp is washed by agitation with water, the oil as it separates from the husks

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[1] For a description of a peculiar form of wedge press used in Formosa for the extraction of olive oil, see Report by Consul Warren on the trade of Taiwan, *J. Soc. Chem. Ind.*, 1891, x., 556.

and rises to the top running off together with water to separation tanks. The residual wet oil-containing husks are strained and boiled down to a kind of porridge or soft pulpy dough, and the oil mixed with water, then separated by pressure in some sort of rough screw-press. In some cases the resulting marc is ground up again by heavy edge-runners of granite, etc. (worked by water or cattle power), boiled up afresh with water, and subjected to further pressing.[1]

A somewhat analogous process is sometimes used in the extraction of the fat or "butter" of the tallow tree (*Stillingia sebifera*), and other vegetable semi-solid oils or fats. The crushed seeds, nuts, etc., are placed in wicker or bamboo baskets, weighed with stones under boiling water, so that the melted fat gradually separates and rises to the top; the remaining oil is then extracted by pressure applied to the still hot material. This method is more particularly suited to those nuts, etc., whose kernel is surrounded by a highly oleaginous pericarp, which is thus melted away by a process closely akin to the "rendering" of animal fats by means of steam or boiling water (*vide* Chap. x.).

Processes closely analogous in general character are in use in various countries for the extraction of oils from fish of various kinds (*e.g.*, sardines), and from fish and shark livers, whilst the mode of preparation of most kinds of wax is very similar. Thus, in the case of Chinese wax (*Peh-la*), the insect producing the wax is a species of *coccus* (possibly several different species), the young brood of which adheres to and punctures the bark and twigs of the trees (*Fraxinus chinensis, Ligustrum lucidum*, etc.) on which it dwells. A waxy material is secreted[2] covering the bark, in which the insects ultimately imbed themselves, forming chrysalides. To obtain the wax, the branches are scraped, some of the cocoons being reserved for breeding, the rearing of the insects being a special industry, like silk growing; the scrapings are heated with boiling water so as to melt off the waxy matter, which is separated by skimming from the dirt, dead insects, etc.

The different kinds of vegetable wax (myrtle wax, Japan wax, carnauba wax, etc.) are, for the most part, obtained in a similar manner by treating with boiling water the berries, bark, etc., in or on which the material is naturally secreted or deposited, and separating the melted wax as it rises. Bees' combs, etc., are similarly treated to obtain beeswax, and separate it from adherent honey and solid impurities.

Elbow Press.—Although the older rude forms of lever press and wedge press have been to a large extent superseded by more modern devices, more expecially by hydraulic pressure, they are still by no means extinct among those peoples where advancing civilisation has not yet entirely improved away the ancient methods and customs,

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[1] Descriptions of the appliances in use in the Maritime Alps and in Southern Sicily for the preparation of olive oil are given in the *J. Soc. Arts.*, November 20, 1891, and June 16, 1893.

[2] As in the case of beeswax, opinions differ somewhat as to how far the wax is originally present in the sap of the trees serving as food, and how far it is formed or altered under the influence of animal life.

whilst improved machines of these classes are still in active use to some extent even in Europe and America. Fig. 41 represents a form of "elbow press," at one time largely used in the United States for expressing hot melted tallow, etc., from animal adipose tissue. As the screw is worked (by hand wheel or band and pulley) the two powerful elbows are straightened, and the ram depressed. Owing to the mechanical nature of the action, the pressure is automatically increased towards the end of the operation as the elbows straighten.

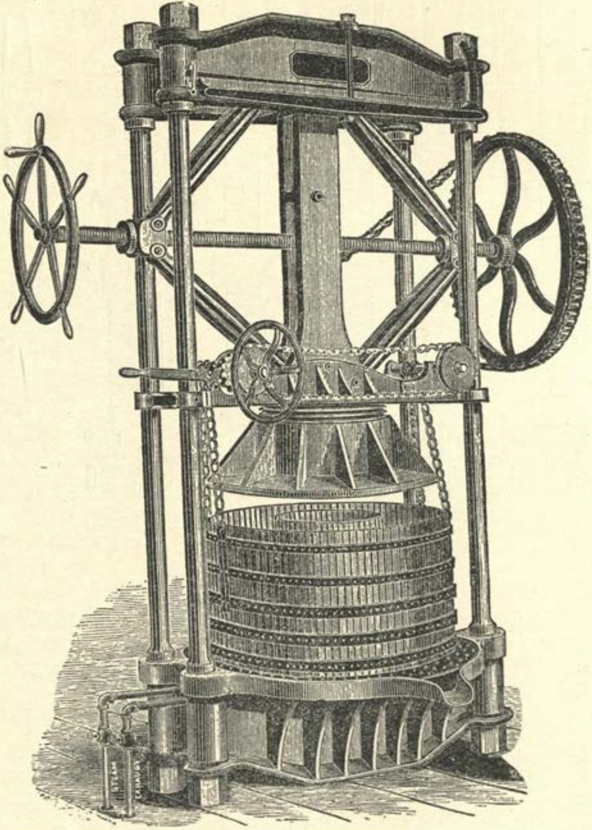

Fig. 41.—Elbow Press.

Wedge Press.—An improved form of wedge press is represented by Figs. 42 and 43 (from *Schädler*) in front and side elevation, Fig. 44 indicating the longitudinal section of the lower portion. Inside each of a pair of troughs, J J, is placed an arrangement of wooden wedges and planking, B L S K B, together with two bags containing the crushed seed, etc., to be expressed, O O, each enclosed between cast-iron frames, T P. The "loose wedges," L L, are suspended by ropes, and serve to lock the whole arrangement together, the loosening, when the pressure is completed, being effected by casting off the ropes and allowing the suspended vertical beams, C C, to descend,

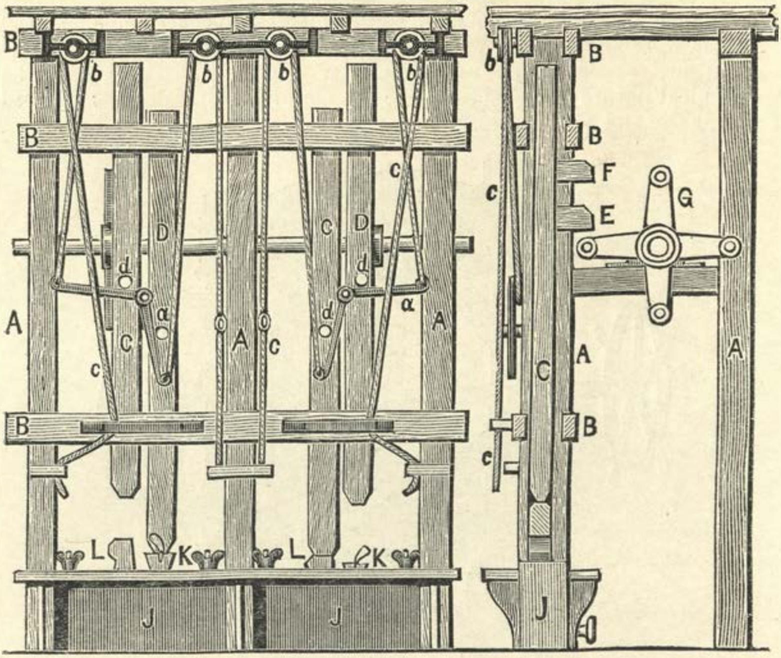

Fig. 42. Fig. 43.

Wedge Press—Front and Side Elevation.

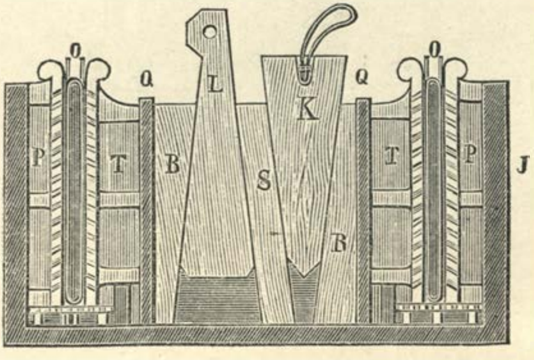

Fig. 44.—Wedge Press—Longitudinal Section of Lower Portion.

pile-driver fashion, so as to drive these wedges, L L, down; A A, B B represent a stout timber frame supporting the driving beams. The pressure is obtained by similarly forcing downwards the "press wedges," K K, by the beam drivers, D D. These drivers are raised by means of stout teeth, G, projecting from a horizontal axle working on studs, E and F, attached to the beams respectively, a system of ropes, *b c*, bent lever, *a*, and studs, *d d*, being attached, so that when the ropes are pulled, either of the drivers can be raised at will, so as to bring it out of the reach of the teeth and keep it suspended out of action. The oil bag, being placed in position between the plates, T P, of the iron frames, L, is adjusted at a convenient height by means of the attached rope. The drivers, D, being then set in action, the press wedge, K, is forced down, and the oil bag consequently strongly compressed. When the oil ceases to run and the wedge is driven home, D is thrown out of action and C allowed to hammer on the loose wedge (the rope attached being slackened); the loose wedge, L, soon falls, and the bags with exhausted oil-cake are then removed and fresh ones substituted.

In some of the Marseilles oil factories an arrangement is in use known as the "Estrayer Cylinder,"[1] the action of which is somewhat akin to that of the wedge press. The apparatus consists of two cylinders, one inside the other, of which the outer acts upon the inner by means of a series of inclined planes, the inner cylinder being composed of eight segments which either close up tightly or separate slightly according as pressure is exercised or removed by the position of the outer cylinder. Screens made of esparto grass and horsehair are employed instead of oil-bags of the same material ("scourtins") such as are employed in other forms of press; these are subject to much less wear and tear than the scourtins, an economy of 80 to 90 per cent. in the cost of the scourtins being thus effected. An interior movement permits the cylinder being enlarged in diameter, so that the cakes can be readily removed. The apparatus will withstand a pressure of 200 kilos. per square centimetre (63½ cwts. per square inch), though half of this is as much as can be safely applied to the ordinary bags without great risk of bursting them. A cylinder holding 80 to 100 kilos. of seeds can be discharged and refilled in seven to eight minutes, the pressing occupying thirty to thirty-five minutes.

Screw Press.—In districts where more modern machinery has not been extensively adopted (*e.g.*, many parts of Spain, China, West Indies, South America, Africa, etc.), rude screw presses are still largely in use in the comparatively small oil mills, where oil is expressed in much the same fashion as has been practised for centuries. Most of these work on the principle of an ordinary copying press, the sacking (or wicker or straw basketing, etc.) containing the material to be expressed being placed between the two plates of the press, and the screw (frequently of wood) turned by means

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[1] *J. Soc. Chem. Ind.*, 1893, xiii., 49.

of a long lever so as to bring the plates nearer together and express the oil, much as a wet sponge would be squeezed in a copying press by turning the handle.

Fig. 45 represents an English improved form of screw press for expressing oil, etc., from fish or similar materials where only a moderate pressure is required. Motion is communicated by belts from shafting to a horizontal axle carrying a worm which gears into a toothed wheel, the revolution of which raises or depresses the screw passing concentrically through the wheel, and consequently elevates or lowers the plunger. According as a straight belt is used connected with one pair of fast and loose pulleys on the axle, or a crossed belt connected with the other pair, the plunger moves in one direction or the other. The material to be pressed is placed in bags between loose metal plates, the press itself being enclosed in a wrought-iron steam casing (stayed to resist pressure) provided with a steam-heated door

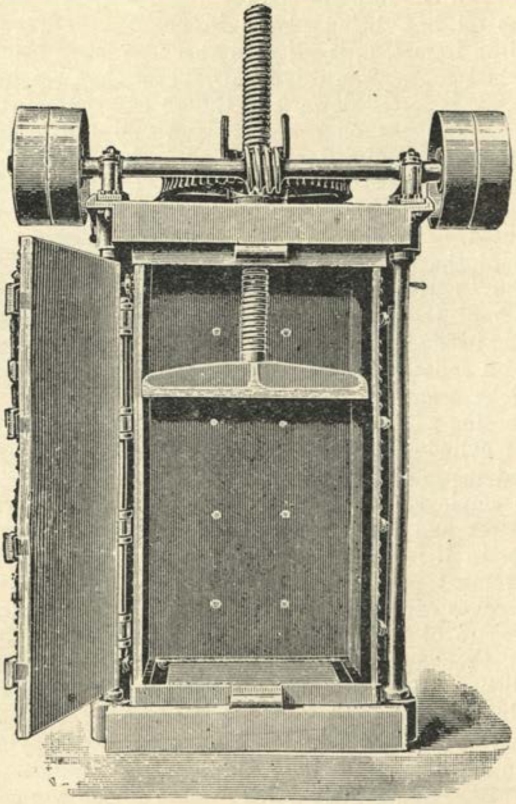


Fig. 45.—English Screw Press.

of similar construction, so that when required the temperature inside the press can be elevated up to that of the steam or nearly so.

Fig. 46 represents a screw press of German make. The material to be expressed is placed inside the perforated cylinder, B, which is then placed inside the cylinder, C, and mounted on the platform, A; the ram, D, attached to the screw, F F, being raised to a convenient height. On turning the horizontal wheel, G, the screw and ram descend and the material is strongly compressed in the inner cylinder. The expressed liquid passes through the perforations in the walls of B and runs out through others at the base of C into a circular groove in the platform, A, and thence by the spout to a vessel placed to

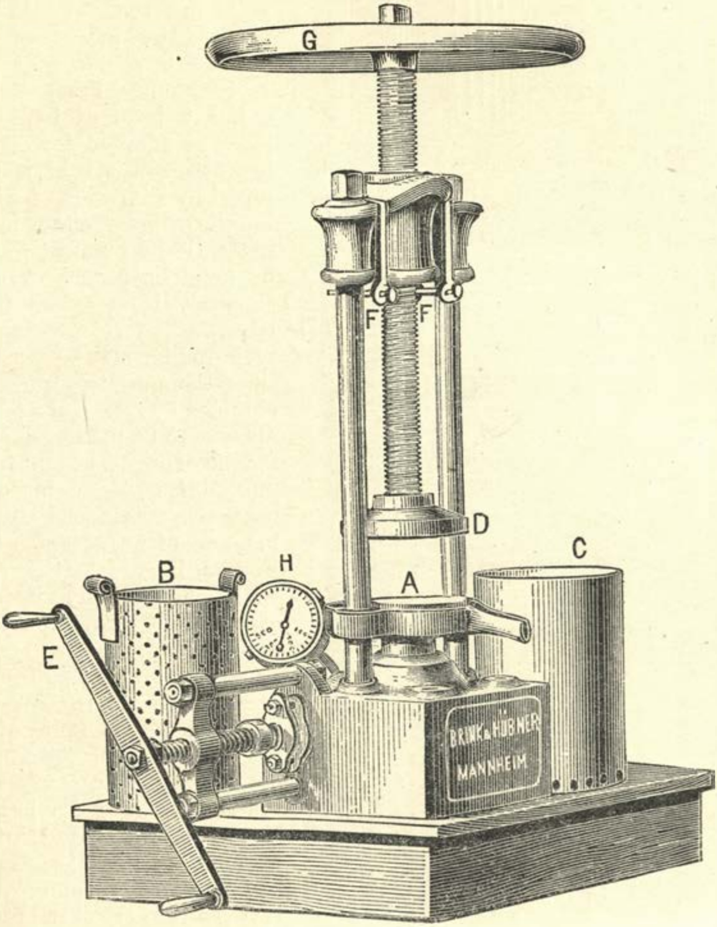


Fig. 46.—Screw Press.

receive it. A small hydraulic arrangement is attached at the base, such that by turning the handle, E, a piston is screwed slowly inwards, thus raising a hydraulic ram on to the top of which the platform, A, is fixed, and so obtaining at the end of the operation a more powerful pressure than would be possible by means of the screw, F F, alone.

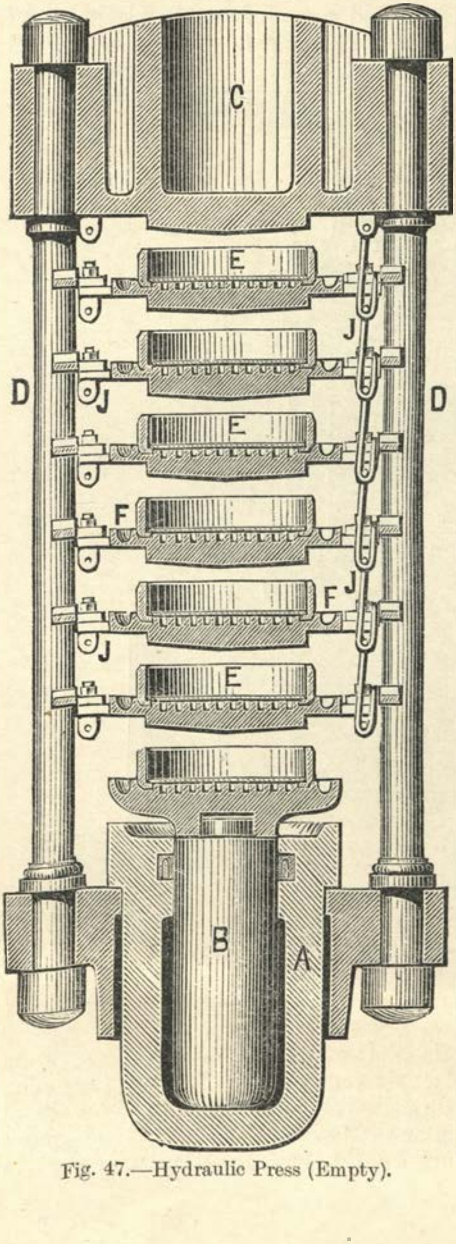


Fig. 47.—Hydraulic Press (Empty).

Hydraulic Press. — The ordinary form of hydraulic press as adapted for oil expression consists of a ram raised by admission of water into its cylinder, either intermittently by pumps (worked by hand or power) or continuously from an accumulator. The former method is preferred for many purposes, since the pulsating pressure obtained by means of a pump appears to be better adapted for the expression of oil from most kinds of seeds, etc., than the continuous steady pressure of an accumulator. Presses in which the ram works horizontally instead of vertically are sometimes preferred. Fig. 47 represents a German form of hydraulic press, empty before charging, and Fig. 48 the same after the ram has risen. The bags are placed in the cavities of the shelves or press boxes, E E E, and the ram started working. As it rises each bag is strongly compressed between the base of the press box containing it and the projecting lower portion of the box next above it; the oil runs out into the circular grooves F, F, and thence to delivery spouts, J J, and so through the pipes G G, to the vertical oil shoot, H, leading to the oil well or tank. The head-piece of the press, C, is supported by stout pillars D, D, to resist the strain.

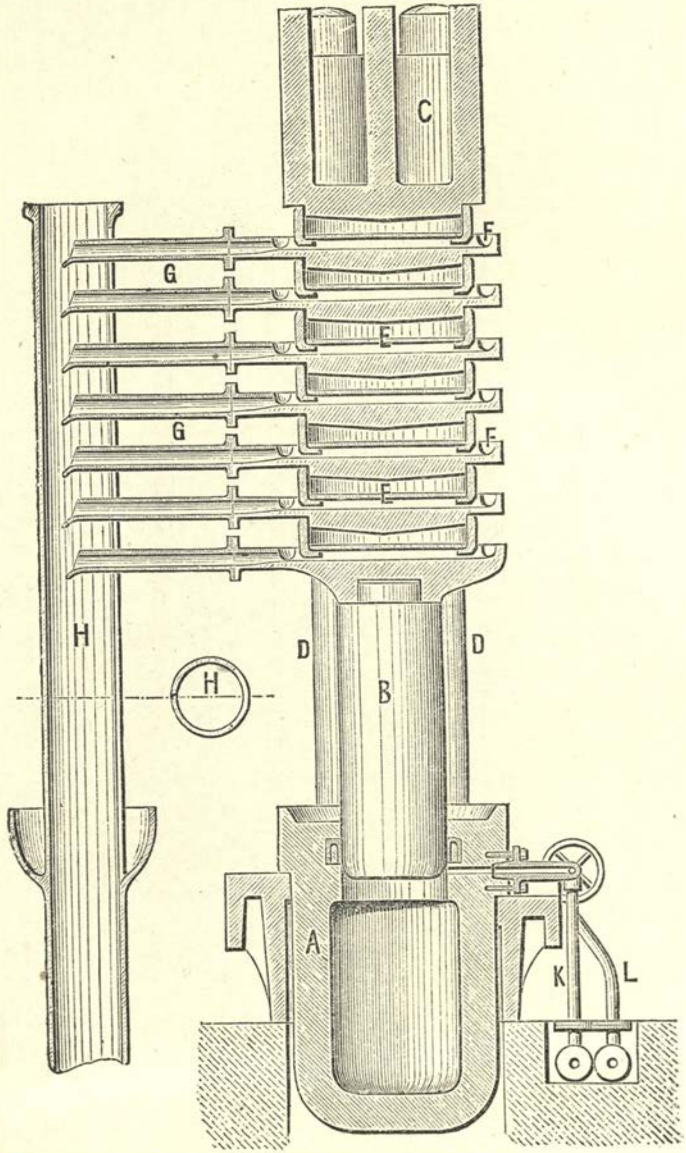


Fig. 48.—Hydraulic Press (after the ram has risen).

Fig. 49 represents an English hand-worked hydraulic press, especially suitable for light work such as that in a small olive oil mill. The press being filled, the larger of two differently sized pumps attached to it is worked by means of the detachable lever handle, until the bulk of the oil is expressed; to obtain a stronger pressure for the extraction of the remainder, the lever handle is then applied to a second smaller pump arranged by the side of the first one, whereby a considerable increase in power is obtained.

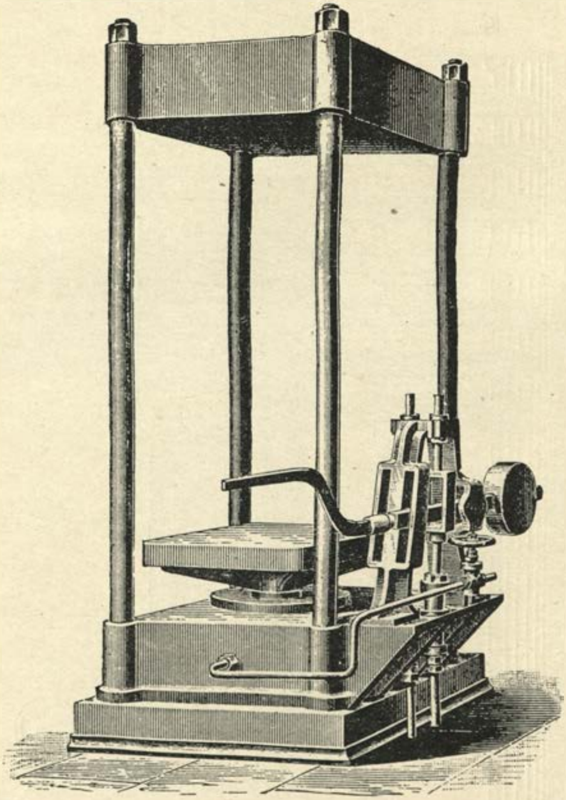


Fig. 49.—Hand-worked Hydraulic Press.

In forms of presses patented by Euston (Eng. Pat. 17,013 and 17,014, 1899) the individual plates can be severally held up or released, or worked in unison with the other plates.

An improved oil press of Eisenwerke (Eng. Pat. 13,623, 1895) has revolving earthenware press-pots used in combination with a seed-heater.

Another apparatus, designed by O'Brien (Eng. Pat. 2,540, 1895), has a series of presses carried on a revolving platform, and the material in each is subjected to pressure from a central accumulator.

Anglo-American System.—Figs. 50 and 51 represent two types of press arranged for working on the "Anglo-American System"

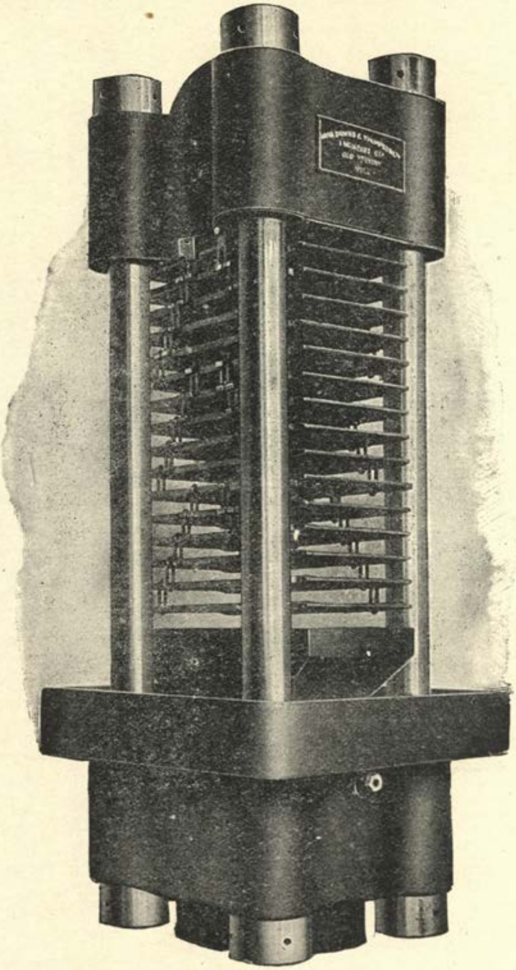


Fig. 50.—Anglo-American Press, with Plates supported by Links.

(*vide infra*). The plates are corrugated, and arranged at such distances apart as just to allow of the moulded cakes of hot ground seed, etc., from the kettle and moulding machine (p. 301) being introduced, preferably from each opposite side alternately. Usually sixteen cakes are pressed simultaneously in one press, while four such presses are worked together in one block, all four being erected inside the same wrought-iron oil tank, which serves as a foundation and collects the expressed oil in a most efficient manner. The pressure employed usually rises from 700 or 800 lbs. per square inch at first up to 2 tons at the end. Figs. 52 and 53 represent two forms of cake plates used in Anglo-American presses, and Fig. 54 shows the cross-sections of cake plates.

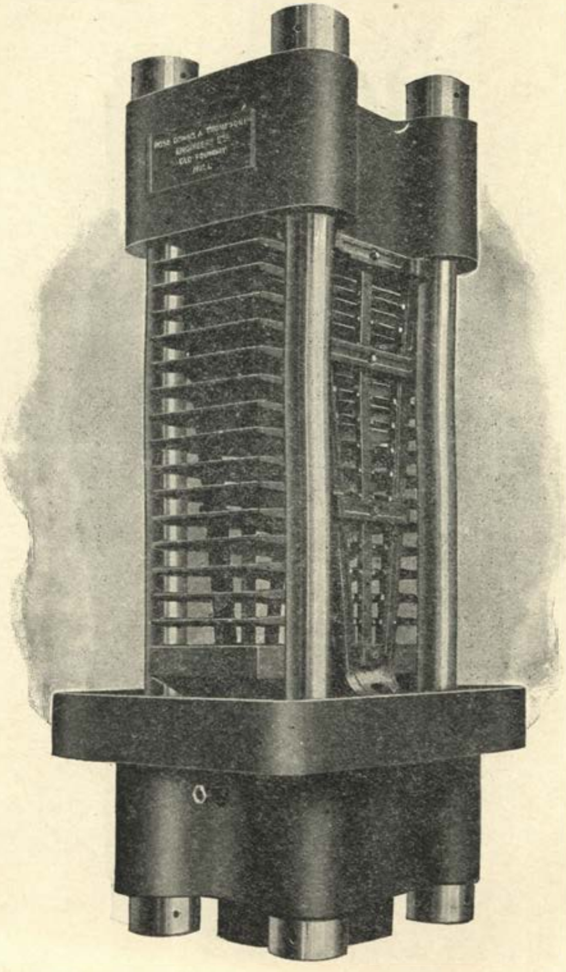


Fig. 51.—Anglo-American Press, with Plates supported by Racks.

A form of horizontal press intended more particularly for expressing cotton-seed without wrapping the material in cloths has been patented by Snypp (Eng. Pat. 16,614, 1899).

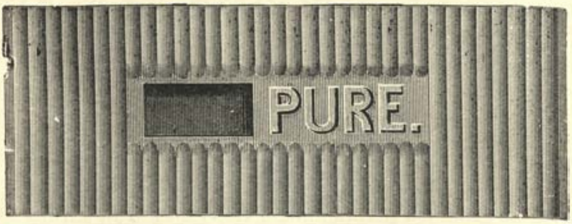


Fig. 52.—Cake Plate, with Removable Brand.

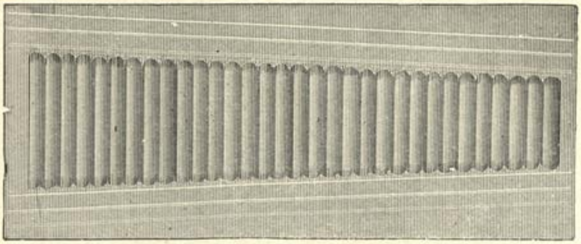
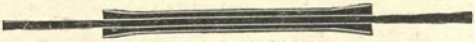
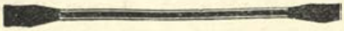


Fig. 53.—Cake Plate to form Taper Cakes.

Flanged built-up Plate.



Plain built-up Plate.



Solid Plate.
Fig. 54.—Cross-Sections of Cake Plates.

"Cage" or "Clodding" Press.—Figs. 55 and 56 represent two types of closed press which are used for the preliminary expression of oil from castor and earth-nut seeds, copra, or palm-kernels. In these presses the meal from the kettle is introduced into a cylinder or cage, either constructed of spaced staves through the interstices between which the oil escapes, or of smooth steel with numerous perforations.

In the press shown in Fig. 55 a regulated supply of meal falls from the kettle press into a chamber which feeds the press, whilst circular discs of metal are placed over the meal. The piston, which is at the top, then falls and allows a fresh quantity of meal to be introduced; another disc is put over this, and so on until the press is charged. On now causing the ram to rise gradual pressure is applied, and the oil escapes through the openings.

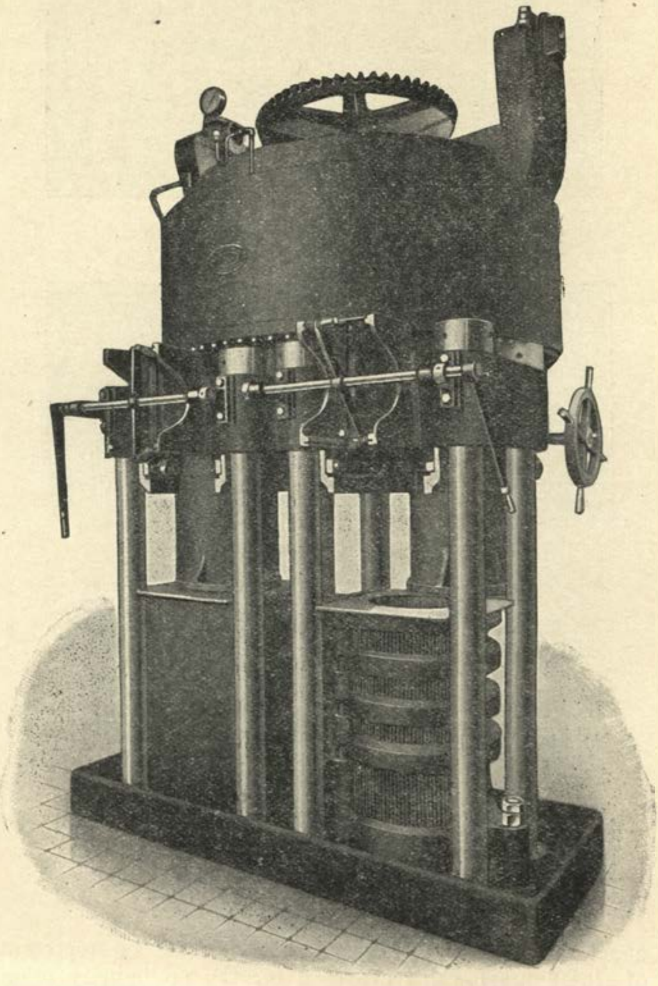


Fig. 55.—" Premier " Press and Kettle.

In another type of clodding press the cage is removable, and can be transferred by means of rollers from the kettle to the finishing press.

Fig. 56 represents a form of clodding press working on the " Leeds "

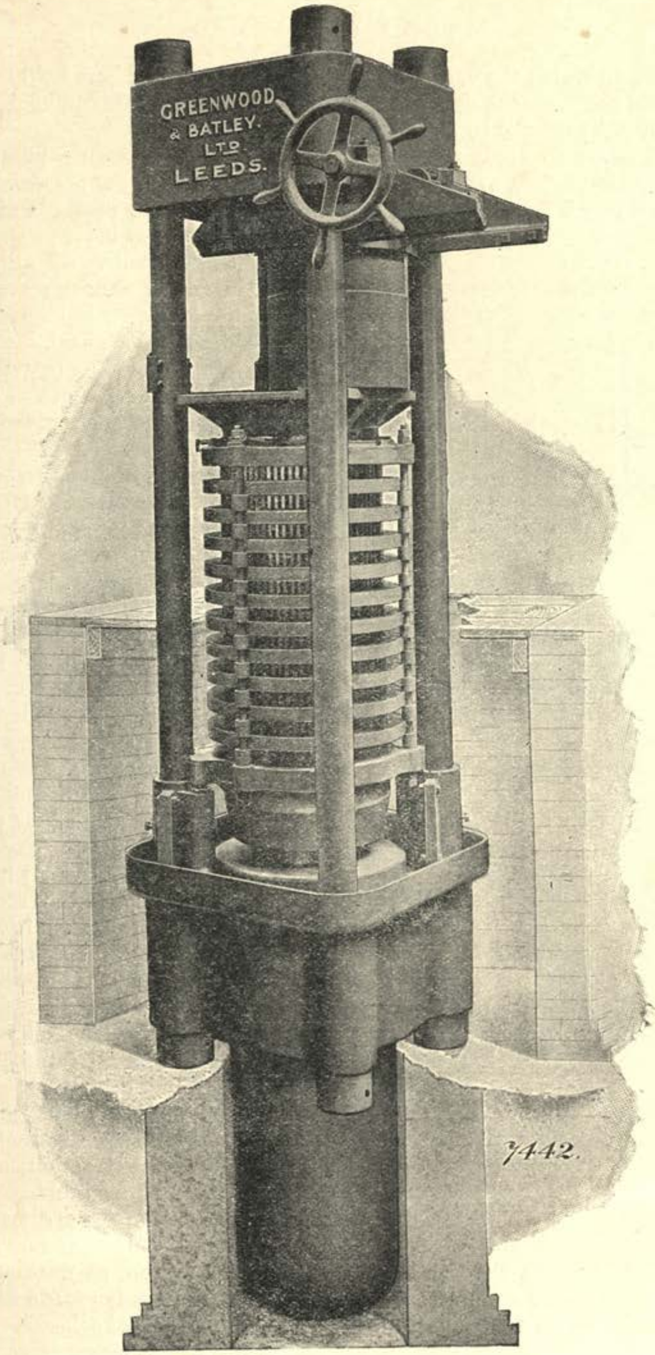


Fig. 56.—Hydraulic Oil Press, "Leeds" System.

system, in which the cages are constructed of vertical bars held together by steel hoops. The sizes of the spaces between the bars can be regulated to suit the material to be pressed.

In order to apply the pressure gradually, low-pressure pumps and accumulators (Fig. 57) are used in connection with these presses. These allow a regulated pressure of from about 800 lbs. to upwards of 4 tons per square inch. They are provided with an automatic device for knocking off the pump when the maximum pressure is attained.

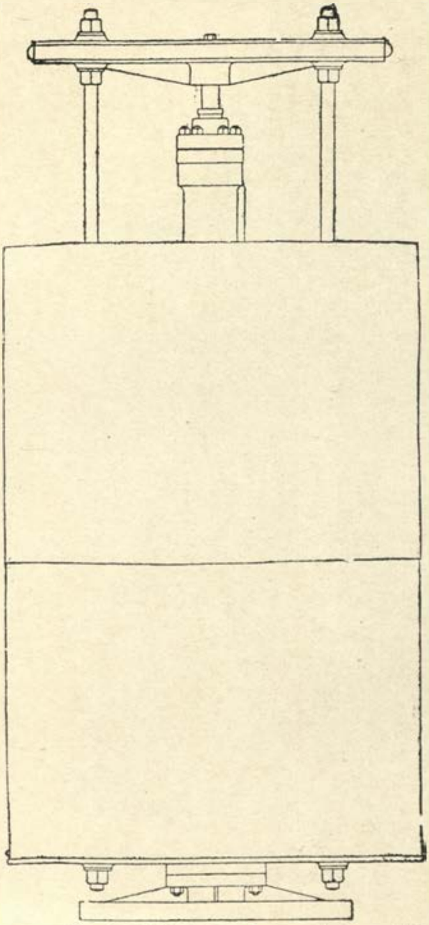


Fig. 57.—High-Pressure Accumulator, with Wrought-Iron Casing, to carry Slag or Sand.

In the case of material rich in oil, such as copra or castor-seeds, clodding presses are frequently used for the first expression, and the second and third expressions carried out either in the same type of press or in a press on the Anglo-American system.

A great saving in machinery and reduction in the amount of labour is effected by the process of *Downs*, *Bellwood*, and *Turnill* (Eng. Pat. 24,856, 1919), in which oil seeds and nuts, especially those rich in oil, such as copra and palm-kernels, are ground or cut up and subjected to dry heat. This may conveniently be done in a steam-jacketed conveyor provided with internal paddles. In this way moisture is removed, and the material is converted into a semi-solid mass from which oil exudes. Part of this oil can be separated by centrifugal force, whilst the remainder may be separated by filtration, followed by extraction of the residue with a suitable solvent.

Oil-Cake.—The dimensions of the oil-cakes produced vary considerably with the size of the oil mill, the system of working, and the nature of the seed, etc., used; the cakes are always made to taper somewhat so as to facilitate withdrawal from the cake boxes. Thus with the smallest mills the cakes may weigh about 3 lbs., and the dimensions may be 14 inches long, and 6½ inches wide at one end and 5½ at the other, the press being constructed to take from four to six such cakes at a time; whilst with somewhat larger mills the cakes may weigh about 4 lbs., being 20 inches long, and 7½ wide at one end by 5½ at the other. Still larger cakes (up to some 30 inches long, and 10 or 11 wide at one end and 7 or 8 at the other) are made in mills of greater magnitude (especially when working linseed), where the scale of manufacture is large enough to enable full-sized presses, etc., to be employed. Such a linseed cake generally weighs from 6 to 13 lbs., averaging about 8 or 9 lbs., according to the source and richness in oil of the seed used. The weight of the pressed oil-cake obtained from a given quantity of seed is obviously the less the larger the yield of oil. When working on the older system the press usually contains only four cake boxes, three such presses being worked by one man and a boy, including paring and storing the cakes; the presses are charged from three to six times an hour, according to the seed used (cotton-seed about four times, linseed five). With some kind of seed (*e.g.*, rape and gingelly) the crushed seed is worked over twice, two presses being employed for the first expression and three for the second—the press cake produced by the first treatment being reground before the second expression, usually by means of edge-runners. Seeds less rich in oil than linseed and cotton-seed yield proportionately heavier cakes for the same weight of seed; as a rule, with the less oleaginous seeds, etc., a better yield is obtained by pressing proportionately smaller quantities at a time, so as to form in all cases oil-cakes of about the same thickness.

With certain kinds of seeds furnishing "salad" oils of finest character, the expression is carried out in three stages:—First of all cold pressure is applied to a moderate extent, whereby a "cold-drawn" oil is obtained of the purest quality (after refining—*i.e.*, removal of mucilage, etc.). Then the cake is again ground, slightly moistened with water, and pressed a second time, somewhat higher pressure being used; the oil thus obtained is cold-drawn oil of second quality. Finally, the cakes are again ground and heated and pressed hot; the oil thus obtained is far inferior to either of the former runnings. The oil-cake thus left often retains a sufficient quantity of oil to render it worth while to treat by some solvent extraction process (p. 314), whereby a still lower grade of oil is ultimately obtained. This mode of treatment in several stages is more especially adopted in the case of higher class edible oils—such as those from the arachis nut, and from sunflower seed; or in the production of the more highly priced oils used for other purposes—*e.g.*, almond oil. Coarse oils, such as linseed, are usually expressed but once, the pulp being heated at the beginning as described below, partly to render the oil more fluid, and partly to coagulate albuminous matter. Some kinds of seeds, however (*e.g.*, sesamé and rape), are generally treated in two stages—*i.e.*, pressed twice successively so as to obtain two qualities of oil. When the cakes are removed from the press, the cloths are stripped off and the edges pared; the parings contain a notable amount of oil, and are therefore ground up and mixed with fresh crushed seed for another batch.

In some cases mixtures of seeds are intentionally prepared and crushed and treated together; in others the seed as harvested is a mixture, two or more kinds of plants being grown together; so that, excepting when the seeds differ sufficiently in size to be capable of separation by sifting, the oil ultimately obtained is necessarily of a mixed character. Partly from causes of this kind, and partly on account of subsequent adulteration, it is difficult, if not impossible to obtain an absolutely pure oil of any given kind in commerce, the only practicable method of procuring a perfectly pure sample being to hand-pick the seeds and express the oil in a small press kept for such purposes. Accordingly, a small press for the purpose of preparing samples of genuine seed oils from time to time is an indispensable part of the equipment of a laboratory where oil examinations are made by comparison of the substances tested with specimens of oils and mixtures of oils known to be themselves unadulterated.

Composition of Oil-cake.—The analyses quoted below are given by *Schädler* as representing the average composition of oil-cakes of various kinds.

According to *Voelcker*, linseed cake made by the older system usually contains from below 10 to about 16 per cent. of oil, and cotton-seed cake from 6 per cent. (undecorticated) up to 16 per cent. (decorticated). Oil-cakes made by the Anglo-American system of working are usually more completely expressed, so as to contain distinctly smaller percentages of residual oily matter than cakes prepared without the aid of a moulding machine. If, however, the expression be carried too far, the value of the cake as cattle fodder is greatly diminished, so that in extreme cases it may be rendered unsaleable.

Oilcake from	Water.	Fatty Matter.	Cellulose and Non-nitrogenous Vegetable Matter.	Ash.	Proteins.	Nitrogen.
Arachis nuts, .	11·50	8·80	31·10	7·25	41·35	6·80
Cotton-seed, .	13·00	7·50	51·00	8·50	20·00	2·90
Rape-seed, . .	10·12	9·23	41·93	6·84	31·88	5·00
Colza, ...	11·35	9·00	42·82	6·28	30·55	4·50
Sesamé-seed, .	10·35	10·10	38·80	9·80	31·93	5·00
Beech-nuts, . .	11·40	8·50	49·80	5·30	24·00	3·20
Linseed, . . .	10·56	9·83	44·61	6·50	28·50	4·25
Cress seed, . .	12·23	7·68	47·00	12·50	20·50	3·00
Cameline-seed, .	9·60	9·20	50·90	7·00	23·30	3·60
Poppy-seed, . .	9·50	8·90	37·67	11·43	32·50	5·00
Sunflower-seed,	10·20	8·50	48·90	11·40	21·00	2·40
Madia, . . .	11·86	7·90	50·00	12·24	18·00	2·50
Hemp-seed, . .	10·00	8·26	48·00	12·24	21·50	3·30
Palm-kernels, .	9·50	8·43	40·95	10·62	30·40	4·50
Coconuts, . .	10·00	9·20	40·50	10·50	30·00	4·50

Free Fatty Acids in Oil-Cake.—*Nördlinger* has found from 6 to 15 per cent. of total fatty matters contained in rape, poppy, earth-nut, sesamé, palm-nut, coconut, linseed, and castor bean cakes; of which the free acids constituted fractions varying from about $\frac{1}{100}$ to about $\frac{57}{100}$.

According to *Dyer*,[1] linseed cake contains, on an average, about 10 per cent. of oil, varying between 7 and 16 per cent. Of this a quantity varying between one-thirteenth and one-fifth usually consists of free fatty acid, the proportion being less the purer the linseed. With some freshly-expressed cakes, free acid is practically absent; on the other hand, with cakes that have "heated" on keeping, the greater portion of the glycerides originally present is decomposed, producing free fatty acids. Obviously, the proportion of free acid formed chiefly depends on the extent to which hydrolytic actions have taken place during storage.

Dyer and *Gilbard*[2] subsequently published the results of their examination of upwards of 1,000 oil-cakes. They found that in freshly-pressed samples the proportion of free acids was comparatively small, in most cases not exceeding 3 to 5 per cent. of the amount of oil present.

In the case of 268 cakes prepared from screened linseed the free fatty acids formed the following percentages of the oil:—Not exceeding 5 per cent. in 170 samples; from 5 to 10 per cent. in 69; 10 to 15 per cent. in 14; 15 to 20 per cent. in 15; and above 20 per cent. in 10.

The average acidity of 71 cakes made from impure linseed was over 15 per cent.

With cakes made from other varieties of seed the following percentages of free acid calculated on the amount of oil were obtained:—Cotton-seed, 5, or less, to 40; rape-seed (46 samples), 7·8; earth-nut (23 samples), 46·0; niger-seed (6), 7·4; and palm-nut meal (5), 6·4.

Olive Oil-Cake.—The following table shows the composition of olive oil-cakes:—

Source.	Water.	Fat.	Proteïns.	Crude Cellulose.	Non-nitrogenous Extractives.	Mineral Matter.
Tunisian,[3] . .	29·98	15·40	3·51	16·04	31·73	3·34
Portuguese,[4] fresh,	27·51	12·69	5·38	...	...	0·98
,, dried,	...	17·51	7·43	...	...	1·35

Walnut Cake.—*Fallot*[5] gives the following analyses:—

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[1] *J. Soc. Chem. Ind.*, 1893, xiii., 8.

[2] *Analyst*, 1895, xx., 241.

[3] Milliau, Bertainçhand and Malet, *Mon. Scient.*, 1900, lvi., 508.

[4] Klein, *Zeit. angew. Chem.*, 1900, 635.

[5] *Chem. Centralbl.*, 1899, ii., 629.

	Cold-pressed.	Hot-pressed (Eight samples).		
	Per cent.	Per cent.		Per cent.
Water, . . .	9·40	4·11 to 15·04	average	11·40
Proteins, . . .	31·79	29·29 ,, 44·87	,,	37·77
Fat, ...	27·17	9·26 ,, 20·06	,,	13·68
N-free extract, . .	20·61	21·96 ,, 33·62	,,	27·75
Crude fibre, . .	6·83	3·11 ,, 9·01	,,	4·56
Ash, ...	4·20	4·36 ,, 5·27	,,	4·77
P_2O_5, ...	1·77	0·40 ,, 2·40	,,	1·71
K_2O, ...	0·87	1·27 ,, 1·59	,,	1·39

OIL MILL PLANT.

The plant in use in modern oil mills varies somewhat in details according to the nature of the material to be treated, and according as the substance is intended first to be submitted to a preliminary cold pressing so as to obtain a portion of the oil as a product of finer quality, and then to hot pressings to obtain lower grades; or to be treated hot at one operation only. Moreover, the climate somewhat modifies the character of the process, inasmuch as many substances can be sufficiently expressed in a tropical climate, without any extraneous heat being necessary, whereas they would require to be artificially warmed in a colder climate to render the oil sufficiently fluid to exude properly by pressure.

Again, the scale on which the operations are to be conducted, and considerations as to relative cost of labour, fuel, animal power (horses or bullocks, etc.), value of oil-cake when expressed as far as practicable, or only to a lesser extent, and whether to be subsequently treated by solvent processes or not, and so forth, have also to be taken into account.

In general terms, however, the plant may be described as essentially consisting of boilers and engines for steam raising for heating purposes and power; crushing machinery (rolls, edge-runners, etc.) for breaking up the material so as to rupture the walls of the cellular tissues in which the oil matter is contained; heating appliances whereby the material (either as delivered from the crushers, or after a preliminary cold pressure, and subsequent disintegration of the partly expressed cake) is subjected to heat for the twofold purpose of rendering the oil more fluid, so as to facilitate expression, and of partially coagulating albuminous matter so as to obtain a purer product; hydraulic presses whereby the expression is effected; and finally, filter presses, refining tanks, settlers, and analogous appliances, whereby the crude oil is refined and more or less completely separated from watery and organic matters accompanying it when first expressed.

Anglo-American System.—What is now generally known as the "Anglo-American system" substantially consists in the use of a selection of particular appliances for the above purposes in conjunction with a special feature—viz., that the crushed material, after damping and heating in a suitable "kettle," is subjected to a preliminary moulding operation so as to shape and compress it into compact thin blocks or "cakes," which are then expressed.

The chief advantages of this system, as employed in the plant constructed by Messrs. Rose, Downs & Thompson, of Hull, are claimed to be as follows, when contrasted with older systems of arranging and working oil mill plant:—

All the machinery is belt-driven; whereby not only is greater economy secured in the cost of gearing and greater facility in erection, but also a considerable saving (about 20 per cent.) in driving power.

The weight of the machinery required to work a given quantity of seed is materially reduced, whilst the process is equally applicable to all oil-seeds and nuts, slight variations in the nature of the rolls, etc. being made in some cases, according to the nature of the seed, etc., treated.

The plant is less bulky, a great economy in space being effected; whilst there is also a large saving (50 per cent.) of labour in the press room.

The oil is more perfectly extracted. Thus, linseed cakes made on the old system usually contain about 10½ per cent. of oil, and those made by the modern process only about 7 per cent., giving an extra yield of oil to the extent of about 3½ per cent. of the weight of the cake.

The bagging required for moulded cakes is subjected to less severe wear and tear than that used in the ordinary process; whilst the costly hair envelopes are altogether abolished. Moreover, the cakes produced have a better surface and fracture, and are better branded when the crushing is effected by rollers than when done by means of edgestones in the ordinary way.

In what is termed a "unit" mill on this system, the plant is capable of crushing from 160 to 200 cwts. of linseed or rape-seed per day, or 155 to 190 cwts. of cotton-seed. The seed passes down a shoot to a series of crushing rolls (usually five in number), thence by an elevator to the kettle, where it is heated; a moulding machine forms it into cakes, which are placed in presses (four standing in one oil tank) and expressed. A paring machine cuts off the oil-containing edges of the pressed oil-cakes; these are ground up under small edgestones and returned to the kettle to be worked over again with a fresh batch of crushed seed. One set of four presses requires three men in the press room and about 45 actual horse-power to work it. For larger mills, this "unit" set of plant is simply doubled, trebled, or quadrupled, and so on, each additional set requiring a further addition of about 35 actual horse-power. In very large installations, where more than two sets (eight presses) are used, a system of accumulators is preferable rather than separate pumps for each set of four presses; accumulators at a lower pressure being also used for

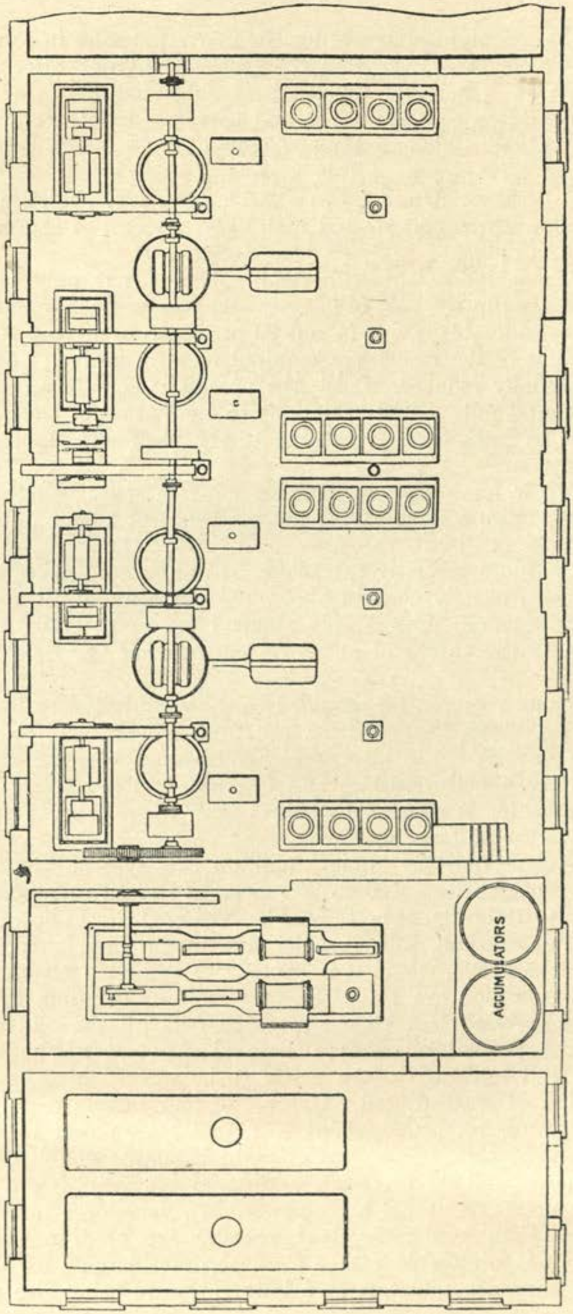

Fig. 58.—Oil Mill Plant; Ground Plan of 16-Press Installation.

the moulding machines, cake hoists, etc., whereby a considerable saving is effected in gearing and space. Fig. 58 exhibits the ground plan of a 16-press installation containing the following plant :—

1 High-pressure accumulator.
2 Low- „
16 Hydraulic presses, each with a hydraulic gauge.
1 Set of hydraulic pumps.
4 Sets of accumulator stops.
4 Sets of seed-rolls (5 rolls in each).
4 Seed kettles.
4 Moulding machines.
2 Paring machines.
4 Sets of elevators.
2 Sets of edgestones.
2 Oil pumps and cisterns.
4 Seed screens.
Oil cisterns to hold 200 tons of oil.
Engine to work to 200 actual horse-power.
Boilers to work up to 250 actual horse-power.

Together with gearing, elevators, sack lift, piping, etc.

Such an installation requires twelve men in the press room, which should measure 66 feet by 44 feet, the whole building being 275 feet by 44 feet, and containing four floors. From 640 to 800 cwts. of linseed or rape-seed, or from 620 to 760 cwts. of cotton-seed can then be treated per day for eleven hours.

Crushing Rolls and Edge-Runners.—Fig. 59 represents a set of five superposed rolls used as described above. These are 42 inches long and 16 inches in diameter, and are so arranged that the seed is delivered from the hopper above (by means of a fluted feed-roller the same length as the crushing rolls, and a slanting shoot), between the two uppermost rolls. Having passed between these, it is delivered by another curved shoot or guide plate on the other side between the second and third rolls, which crush it further ; and in similar fashion it passes by another guide plate between the third and fourth,—then between the fourth and fifth rolls, where it receives the final grinding. The seed is thus crushed four successive times in its passage through the rolls, which are brought into contact by a combination of a screw and india-rubber springs, thus giving a smooth and easily regulated pressure. A much more complete and perfect grinding is thus effected than is possible with single pairs of rolls and edgestones of the older construction. For small installations the rolls used are similar in character, but of proportionately smaller size. Thus a set of four rolls (crushing the seeds thrice successively), each 15 inches long and 12 inches in diameter, suffices for a steam-driven mill of about half the capacity of a " unit ; " and one of three rolls (giving two successive crushings), each 8 inches long and 8 inches in diameter, for smaller sizes still, driven by bullock power.

In some oil-crushing establishments heavy edge-runners are preferred to rolls for certain kinds of material—*e.g.*, Egyptian cotton-seed and copra. Fig. 60 indicates a belt-driven pair of stones, 8 feet in diameter and 20 inches thick (the face being chamfered to 16 inches) ; with these, about 6 tons of Egyptian cotton-seed may be crushed in eleven hours. The best stones are made of well-dressed Derbyshire gritstone, free from all sandholes, cracks, shells, and other imperfections, the bed-stone (6 feet 6 inches in diameter and 22 inches thick) being of the same material.

Smaller sized stones suffice for grinding cake-parings. For the 4-press "unit" installation above described one set of stones suffices,

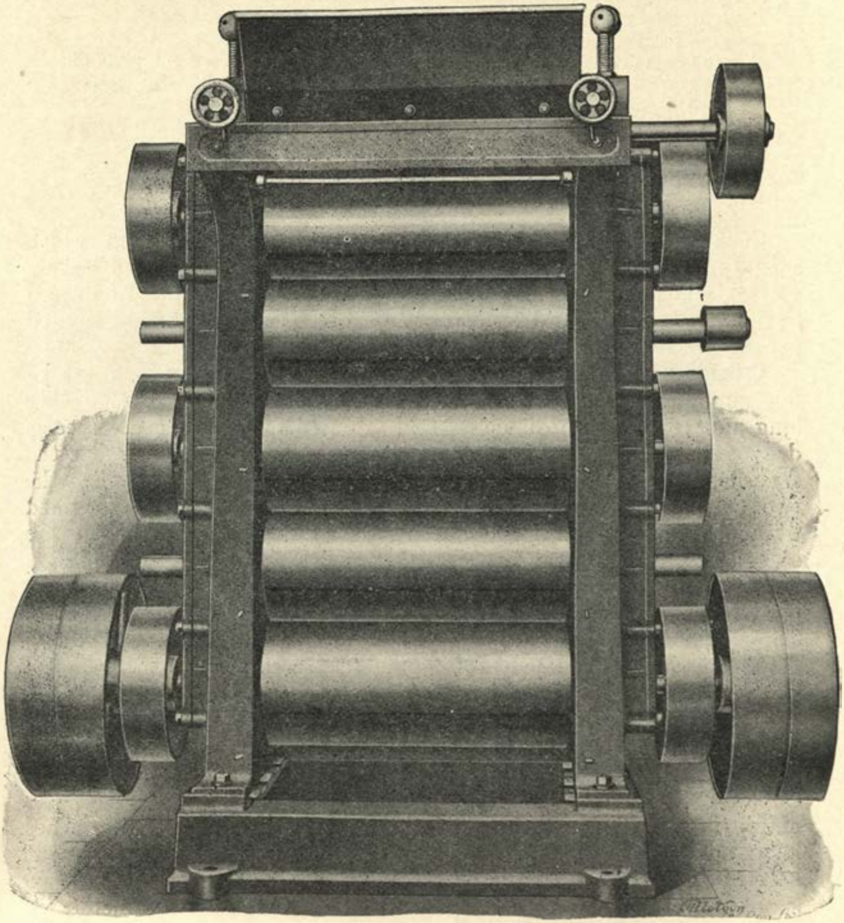

Fig. 59.—Anglo-American Rolls (driven from both ends).

4 feet in diameter and 12 inches thick (face 9 inches). For this purpose, two carfe plates are used instead of one, as shown in Fig. 60, the upper one being perforated, so that the material that is being ground may pass through on to the lower one as soon as it is sufficiently pulverised; from the lower plate it is gathered together and dis-

charged through a shuttle at any convenient point. The texture of the material thus ground is regulated by the fineness or coarseness of the perforations. In some mills working copra, slicing or rasping machines are employed to cut up the material before grinding; but so much damage is done to the knives by stones mixed with the copra that this previous treatment is now but seldom employed, special disintegrators being used instead (p. 306).

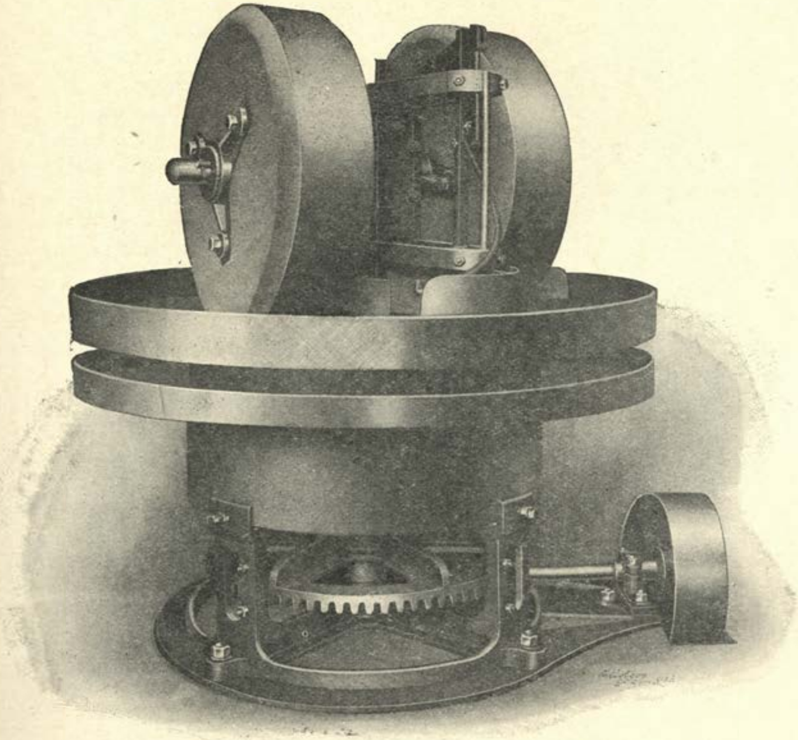

Fig. 60.—Edge-Stones.

Kettle.—The "kettle" used in the Anglo-American system consists of a steam-jacketed circular cast-iron vessel, furnished with an agitator (Fig. 61) driven by a belt. A steam damping apparatus with perforated boss is fixed inside, so that the crushed seed delivered into the kettle by an elevator is moistened by the condensation of steam from the damping arrangement, and heated up uniformly as the mass is stirred by the agitator. By means of a slide at the bottom the heated substance is delivered into a box supplying the moulding machine. The kettle body is fitted with a wooden frame, and covered over with felt or slag-wool enclosed within iron sheeting to keep in the heat. In order to save space, the crushing rolls are sometimes arranged vertically above the kettle; but in addition to the inconvenience caused by this elevation as regards inspection and adjustment, the steam from the kettle is apt to condense on the rolls and clog them; so that this disposition is generally abandoned in the newer mills, the crushed seed being delivered into the kettles by means of elevators or screws, and not by gravity.

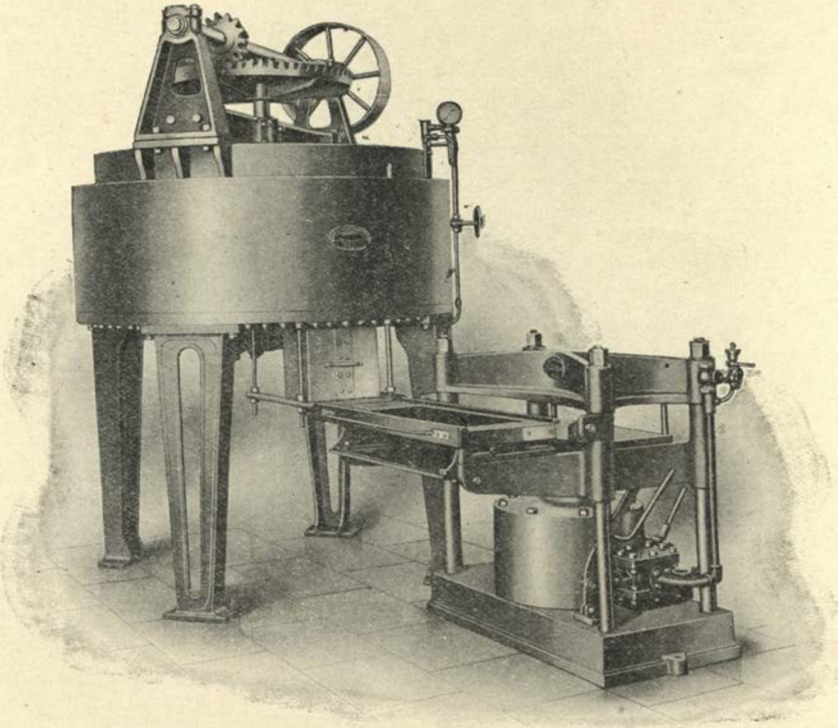

Fig. 61.—Belt-Driven Anglo-American Kettle and Steam Moulding Machine.

In the older system of working where moulding machines are not employed, the kettles used for heating the crushed seed, etc., are of similar character, but are usually not supplied with a damping arrangement, as the necessity for moistening the material in order to mould it better does not then arise.

Moulding Machine.—The use of this appliance is the most distinctive feature of the Anglo-American system. The differences between this and the older method of procedure may be thus stated. In the old system from 11 to 16 lbs. of seed are placed by a boy in a woollen bag; the press-man takes up the bag, doubles it back so as to close the mouth, and then places it on the lower half of a "hair" or other envelope[1] (Fig. 62) that he has previously placed on a table in front of the press. He next smooths the bag with his hand until the seed is distributed throughout the interior as equally as possible. The envelope is then closed over the bag, and the whole taken up and placed in the press. This process is continued until the press is filled, each cake, together with its box, occupying a vertical thickness of upwards of 10 inches. When the moulding machine is used, each cake with its plate only occupies 3 inches, thereby greatly increasing the capacity of the press; whilst the cost of labour is considerably lessened.

The moulding is thus effected:—The workman begins by raising a measuring frame and placing underneath it a sliding frame holding a tray on which is placed a piece of woollen cloth about double the length of the tray centre to centre, the ends of the cloth hanging down. The measuring frame is now brought down on the top of the tray and cloth, and crushed seed introduced from a box (fed automatically from the kettle as required) until the frame is full. The frame is then thrown back, the loose ends of the cloth folded over the seed, and the sliding frame carrying the tray, seed, and cloth pushed forward over the pressing plate. This motion of the frame sets the machine at work, the pressing plate ascending and squeezing the seed into a compact mass about 1¼-inch thick, after remaining in contact with it about a quarter of a minute. The pressing plate then falls, and the machine stops, enabling the press-man to remove the compressed cake to the press, carrying it on the tray which is withdrawn as soon as the cake is in position. During the time that the cake is being compressed, the moulder is engaged in forming another one on a tray in front of the machine as before; so that cakes to the number of 240 may be thus moulded in an hour.

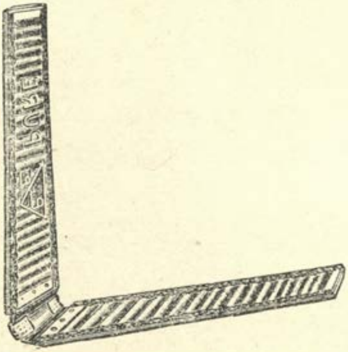

Fig. 62.—Envelopes.

Fig. 61 represents a moulding machine actuated by steam in position with respect to the kettle; other forms are sometimes used worked by hydraulic power.

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[1] Envelopes of vulcanised fibre, paper, and other materials are frequently employed instead of the more expensive "hairs"; and in an apparatus patented by Euston (No. 17,013, 1899) the plates of the press are provided with a rim at the front and the sides, leaving a space for the oil to run out at the back, and thus dispensing with any envelope between the cake and the metal.

Paring Machine.—The cakes obtained in the hydraulic press are usually oily at the edges where the oil exuded, so that the edges require to be cut off, not only to trim the cakes, but also to save the oil with which they are impregnated, the parings being ground up and returned to the kettle. In mills working on the older systems, the press-cakes are generally trimmed by hand; but the simple form of machine indicated in Fig. 63 not only enables the parers to do much more work in a given time, but also to cut the edges far more regularly and neatly.

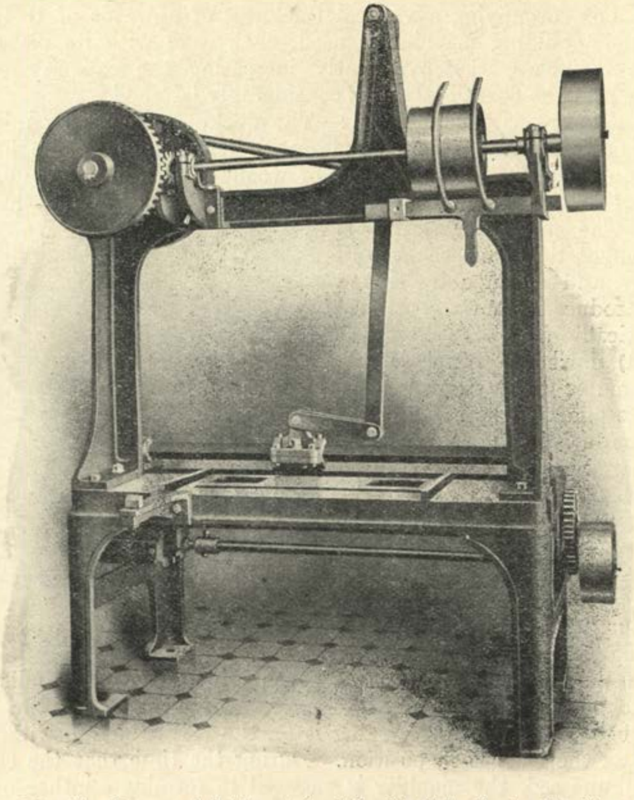

Fig. 63.—Improved Self-contained Double Cake Paring Machine.

The cake to be pared is placed with one edge over a central longitudinal trough; a cutter block with attached knife passes along and shears off the portion of the cake projecting beyond a given line, being driven by the eccentric working a bar jointed to the upper part of the frame. The other side and ends of the cake are trimmed in the same way, two knives being attached to the cutter block, one cutting when the motion is in one direction, the other when in the opposite direction. A screw works in the trough, so that as the parings fall they are carried onward by the screw and delivered on to the upper carfe plate of a pair of edgestones (Fig. 60), whereby they are reduced to meal, which is then taken up and distributed to the kettles by elevators and screws.

Supplementary Appliances.—In addition to the preceding principal appliances, various other minor arrangements are necessary in a well-appointed oil mill. Thus, screens of various sizes of mesh are required to sift out stones, etc., and partially to separate different kinds of admixed seeds when their respective dimensions render this practicable. Machines for decorticating seeds are also employed. Fig. 64 represents cotton-seed treated by such a machine. A indicates ordinary Egyptian seed coated with cotton filaments; the machine cuts through the husk and kernel, B; a separator then divides the husks, C, from the

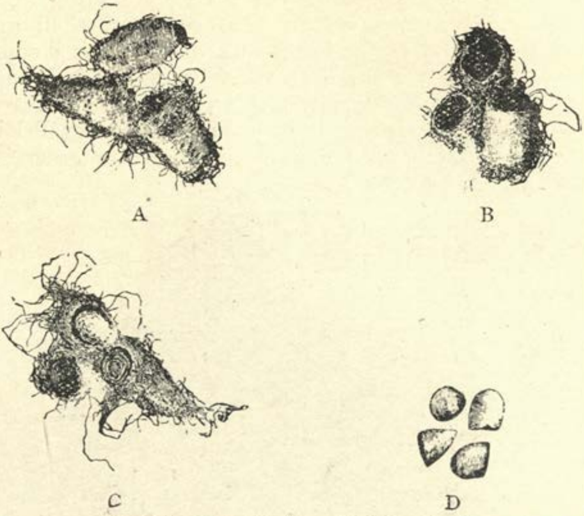

Fig. 64.—Decortication of Cotton Seeds.


Fig. 65.

Fig. 66.

Figs. 65 and 66.—Decortication of Castor Beans.

oily kernels, D, the latter being crushed and expressed, and the former used for manure, etc. Similarly, castor beans are contained in an outer shell (Fig. 65); a special castor seed-decorticating machine removes the outer shell (Fig. 66, A), leaving the white kernel, B, ready for the press.

Analagous machines are employed for decorticating arachis nuts and for splitting coconuts, cutting through husk, shell and kernel at one operation; and for grinding and disintegrating copra. Pulverising machines for this purpose, where the action is brought about by a series of blows from rapidly-moving flat beaters, answer better than those where the grinding is effected between parallel iron discs by friction. Fig. 67 shows a type of disintegrator extensively used in Ceylon for grinding copra.

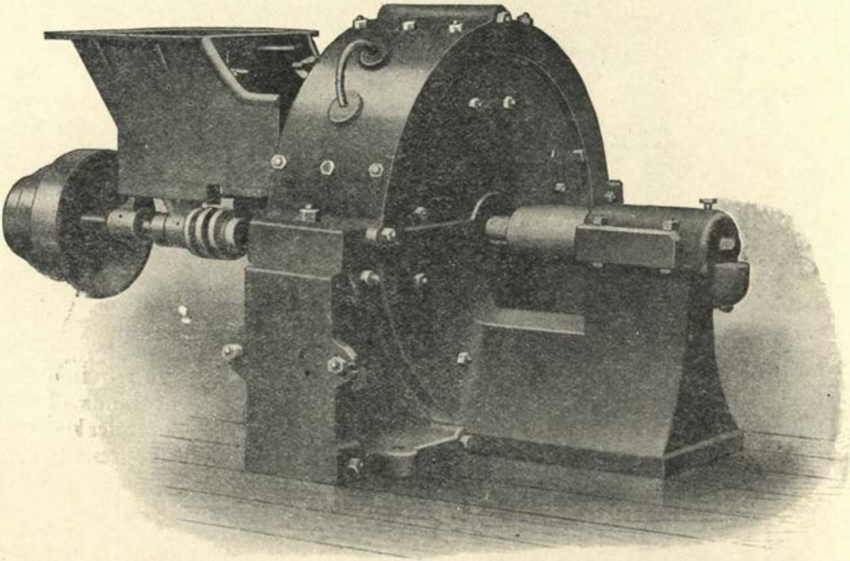

Fig. 67.—Disintegrator.

Chemical Decortication of Cotton-seed.—*Dudley* and *Perry* have patented a process[1] for chemically decorticating cotton-seed. The seeds, after linting, are subjected to the action of gases containing nitrous anhydride and sulphur dioxide, with enough air to "regenerate" the higher oxides of nitrogen as fast as they are reduced. After a few seconds' exposure the fibre has changed but little in appearance, but its structure is completely destroyed, so that the slightest friction causes it to fall to an impalpable powder, leaving the seeds perfectly smooth, and showing no signs of corrosion. A slight

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[1] U. S. Pat. 344,951.

acid reaction is perceptible on the outside, but is readily removed by washing; no acid penetrates into the interior.

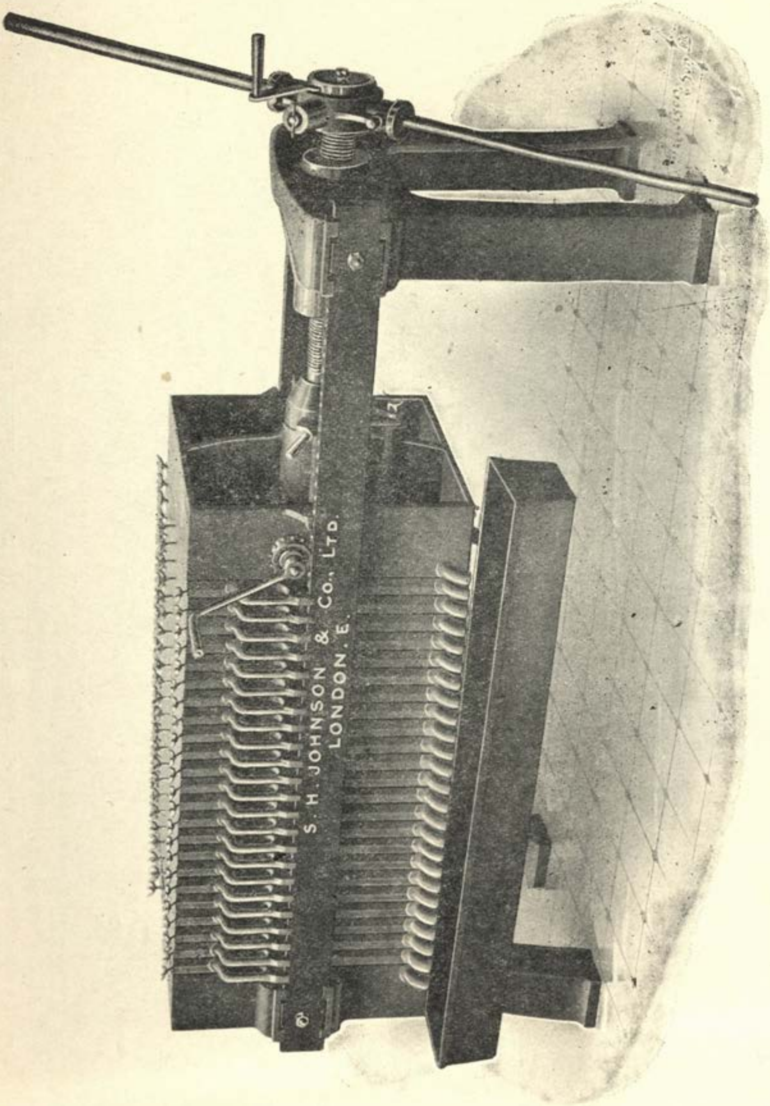

Fig. 68.—Filter-Press for Crude Expressed Oils.

Filtration of the Oil.—The crude expressed oil carries with it more or less watery matter, together with mucilaginous and albuminous organic substances, requiring processes to be adopted for their removal. Formerly these generally involved long-continued standing, so as to enable the solid impurities to form and settle, the process being

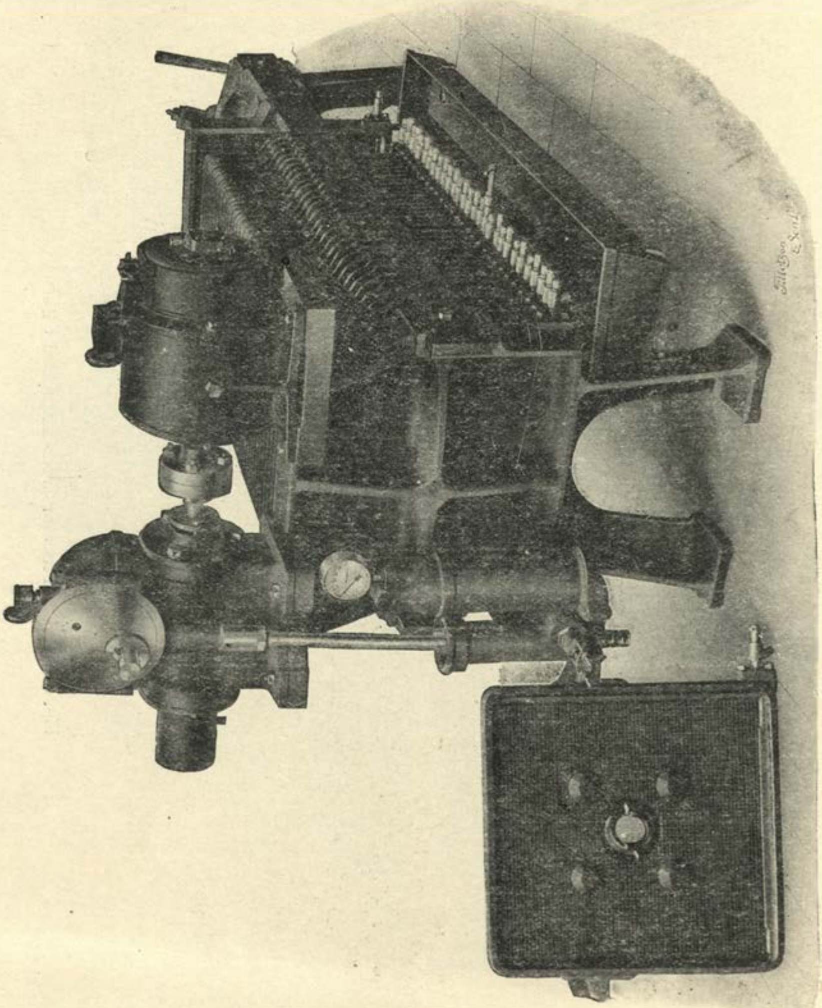

Fig. 69.—Filter-Press with Electrically-Driven Pump.

in some cases hastened by heating to coagulate albuminous matter, or by the use of chemicals (*vide* Chap. XI.). In many cases, however, it is found that a degree of clarification sufficient to render the oils immediately saleable, can be readily effected by simply pumping the oil (either just as it runs from the press into the oil-well, or after heating to a temperature somewhat short of 100° C. to coagulate mucilage, etc.) through a filter-press. The substances thus filtered out from the oil are generally returned to the kettle and worked over again with a fresh batch of crushed seed, so that the only products finally obtained are filtered oil and pressed cake, no "foots" of any kind being made.

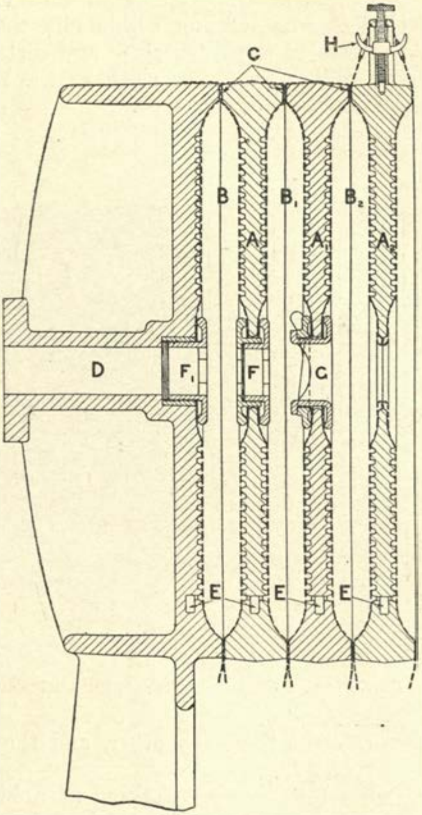

Fig. 70.—Section of Filter Cloths, showing Methods of Fixing.

In the case of many kinds of oil, this simple treatment refines the oil sufficiently for most purposes; in other cases, although subsequent refining methods are still necessary, yet, on account of the previous removal by filtration of a large proportion of the impurities, the rest of the refining process is much facilitated and shortened. Accordingly, in the newest installations suitable filter-presses form an important part of the subsidiary appliances employed.

Filter-Presses.—Fig. 68 represents a filter-press such as is used for the filtration of the crude expressed oils. The filter plates are of the " recessed " type, the faced rims standing above the filtering surface, so that when in position in the press hollow spaces or chambers are formed between the adjacent plates, which eventually become filled with the solid matters filtered out from the oil. Fig. 69 shows a filter-press fitted with a self-contained electrically driven pump; belt-driven and steam pumps are also provided. Fig. 70 is a sectional diagram of a part of a filter-press showing plates with different methods of fixing the filter cloths. For refining edible oils the latest practice is to employ filter-presses of the flush plate and distance frame type, using filter paper in addition to filter cloth as the filtering medium. Fig. 71 illustrates a filter-press of this type.

All these filter-presses have a filtering surface of the " Pyramid " type, which is more efficient than any other, and the special features of which are shown by Fig. 72.

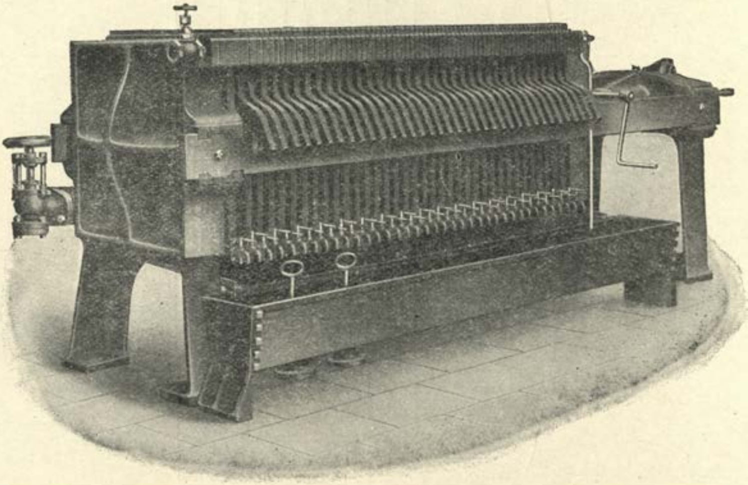

Fig. 71.—Filter-Press, with Flush Plates and Distance Frame.

For special purposes filter-presses working at a high pressure are sometimes employed, the machine represented by Fig. 73 being suitable for a working pressure of 300 lbs. per square inch.

Of patent modifications connected with filter-presses, mention may be made of the following:—

In a special form of filter-press designed by *Dehne* and *Harzer* (Eng. Pat. 575, 1894), the deposit can be washed from the cloths without taking the press to pieces, a current of water being sent through them in a reverse direction to the filtration.

A form of filter-press recently patented by *Mackenzie* (Eng. Pat. 13,901, 1900) has means provided for the oil to pass through the plates instead of over them. The plates consist of an upper and lower part connected by an intermediate wrought-iron plate. The external surfaces are corrugated, whilst the inner surfaces have channels communicating with holes in one of the outside parts.

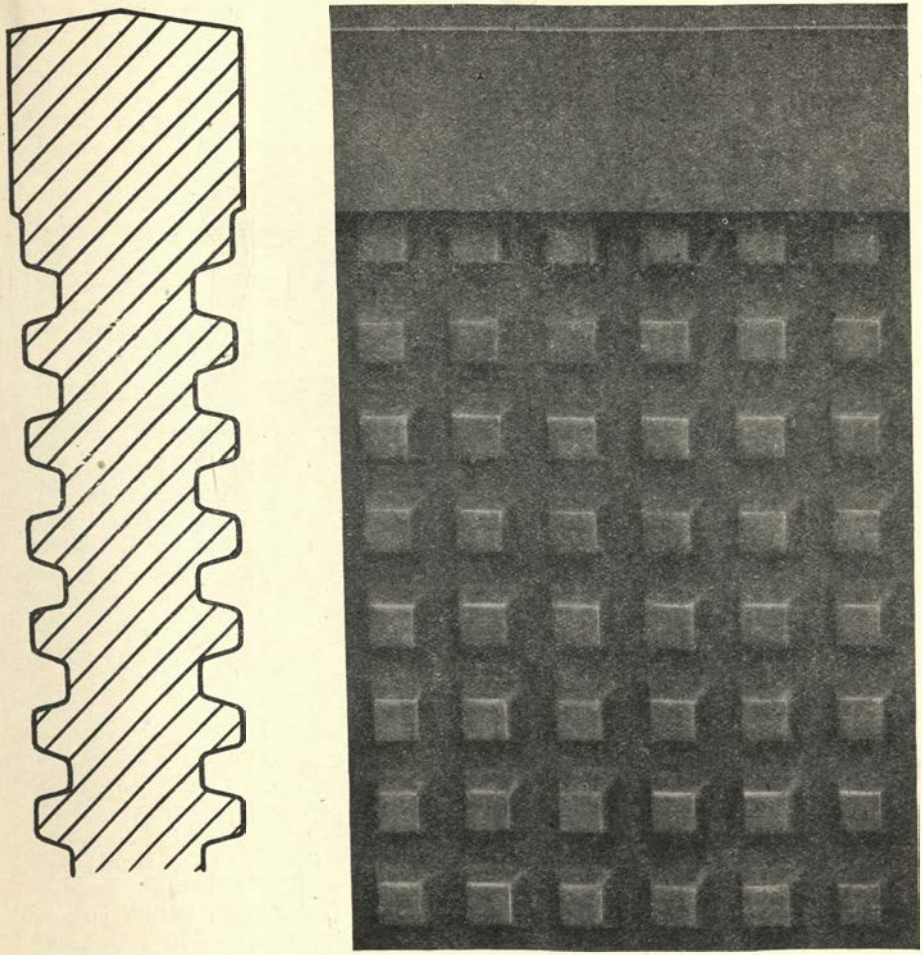

Fig. 72.—Pyramid Surface of Filter-Press.

To prevent unequal wear, *Bastiaans* (Eng. Pat. 7,718, 1896) makes use of filter cloths in the form of flattened tubes, which can be refolded so that the opposite sides are in different relative positions.

Another type of filter-press, patented by *Bonnvillain* (Eng. Pat. 13,562, 1900), has a pressing box formed of superposed rings, each of which has a circular groove for a filtering wick, with radial passages for the expressed oil.

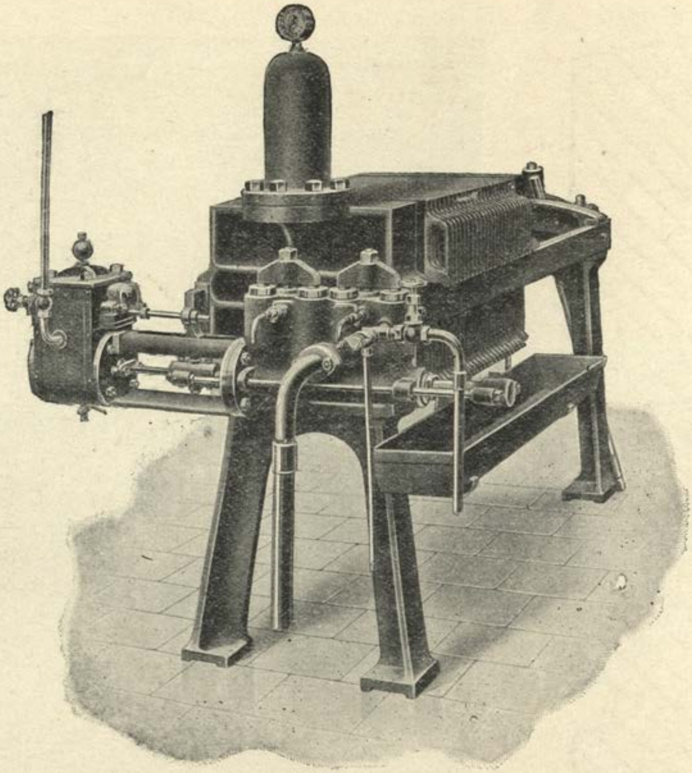

Fig. 73.—High-Pressure Filter Press.

SEPARATION OF SOLID STEARINES FROM OILS, ETC.

Many oils when allowed to stand for some time at a sufficiently low temperature deposit more or less solid matter, sometimes becoming semi-solid or buttery in so doing. If the temperature be raised, the whole mass melts again to a fluid oil; but by "bagging" (or straining off the liquid portion through canvas bags forming rough filter-strainers) without applying heat, the solid matter may be collected; and by applying pressure to the "bagged" mass the remaining liquid may be squeezed out. When the solid matter thus collected is sufficiently granular, the ordinary method of cold pressing may be conveniently applied, the process being carried out in much the same way as that described above in the case of crushed seed-pulp, excepting that the pressure is applied more gradually and gently; but in many cases the solid particles are so fine that they are to a large extent forced through the interstices of the press cloth (even when specially made cloths are employed) and thus lost in the liquid runnings. In cases where the solid matter is present in too small quantity for ordinary cold pressing, filter-presses may often be conveniently employed to collect and consolidate the solidified constituents. Thus olive oil, when cooled for some time, deposits a considerable fraction of the more solid glycerides contained (palmitin, stearin); these, when collected by the filter-press, furnish an "olive stearine," whilst the filtered oil is proportionately less liable to thicken and yield a deposit in cold weather. In like manner, cotton-seed oil furnishes a considerable amount of "cotton stearine" and a more fluid liquid oil, known in consequence as *winter oil*. Animal oils, such as cod-liver oil and whale oil, furnish analogous stearines; from sperm oil, spermaceti is similarly separated.

In the manufacture of paraffin wax for candle-making, etc., certain fractions of the distillates obtained consist of mixtures of hydrocarbons of different melting points, some fusing at considerably above the ordinary temperature. On chilling such "oils" by means of a suitable machine, the hydrocarbons of higher melting point mostly separate in the solid form, so that by straining the magma, or subjecting it to filter pressure, the solid paraffins are separated from those yet liquid. The solid matters thus obtained (paraffin scale), when refined, redistilled, and subjected to further pressings at regulated temperatures, ultimately furnish "paraffin wax" of melting point the more elevated the higher the temperature at which the last warm pressing has been effected, this temperature being regulated by the nature of the material dealt with, some kinds of distillates furnishing paraffin wax of higher melting point than can be isolated from others.

Similar operations are used in various other manufactures connected with the coal-tar and mineral oil industry; thus the separation of carbolic acid from mixtures of that substance and its homologues and other bodies accompanying it, is effected by chilling by means of an ether or ammonia freezing machine, and draining off the unfrozen liquid from the mass of crystals that gradually forms. In like manner, "anthracene oils" obtained at a certain stage of coal-tar distillation become more or less pasty and semi-solid on cooling and standing; so that, by straining off the liquid portions (by filter pressing or otherwise) and subsequently expressing the remaining liquid by more powerful pressure, a solid residue is ultimately obtained, consisting of anthracene intermixed with other solid hydrocarbons, etc.

In the manufacture of "stearine" for candles (stearic and palmitic acids, etc.), analogous methods are used to separate the solid fatty acids that have crystallised into a honeycombed mass, the interstices of which are filled with the liquid acids ("red oils"). Hydraulic pressure of the spongy solid mass in sacking serves to effect a first separation of matters respectively solid and liquid at the ordinary temperature. Further "hot pressing" at a more elevated temperature brings about a more complete elimination of liquid acids from the crude once-pressed stearine; whilst by chilling the red oils, a separation of part of the solid acids dissolved in them takes place, so that, by filter-pressing the mass, fluid red oils run through, whilst an additional quantity of impure solid acids is retained on the filter cloths.

Manufacture of Lard Oil and Allied Products.—At the ordinary temperature of 15° to 25° C., lard constitutes a soft mass consisting of two kinds of matter—one solid and one fluid; it is, in fact, an exaggerated case of the mechanical separation from one another of two constituents of a mixture possessing different solidifying points when the temperature is maintained between the two temperatures of fusion, chiefly differing from the partial solidification of fluid oils on cooling and standing in that the solid constituent has a higher melting point, and is present in larger quantity. By placing the lard in close-textured woollen bags supported by wickerwork frames, and subjecting it to long-continued cold pressure (about 10 cwts. per square inch, lasting for some eighteen hours), the fluid constituent is gradually expressed and the solid retained. The former is known as "lard oil," and constitutes about three-fifths of the whole; the latter is "lard stearine," and is a valuable material for the preparation of the better kinds of soap.

Coconut oil and other analogous vegetable semi-solid oils or butters can, in like manner, be separated by pressure into a fluid "coconut oleine," and a solid "coconut stearine;" and in similar fashion, the fats of lower melting point obtained in the first process for the manufacture of margarine, solidify at a suitable temperature to a semi-solid mass, which, when carefully pressed, yields a fluid portion becoming of a buttery consistence when cooled a little further, and a solid stearine suitable for candle- and soap-making. Fats of greater solidity at ordinary temperatures, such as tallow, when similarly expressed, also separate into two portions—*e.g.*, liquid "tallow oil" and solid "tallow stearine."

EXTRACTION OF OIL FROM SEEDS, OIL-CAKE, ETC., BY SOLVENTS.

Most oily matters are extremely soluble in benzene, light petroleum distillate, ether, chloroform, carbon bisulphide, carbon tetrachloride, and other readily volatile solvents; so that, by bringing such fluids in contact with the material to be treated, the fatty matter is dissolved, whilst the other constituents are, for the most part, unaffected. By drawing off the solution and subjecting it to distillation, the solvent is volatilised, and with proper condensing arrangements can be regained with but little loss for use over again, whilst the oil remains in the still.

A large number of different arrangements have been proposed, and many are in actual use (more especially on the Continent) for effecting this purpose, differing in various respects according to the nature of the material to be treated and the solvent employed, etc. When the material is rich in oil—*e.g.*, when palm-kernels (ground to meal) are used, and similar substances not already largely deprived of oil by expression, the apparatus employed consists essentially of a cylinder or other closed tank of boiler plate, provided with a manhole for charging and discharging the meal, which is supported on a perforated false bottom. Into this carbon bisulphide is run by gravitation, or pumped from a well, entering at the bottom and passing upwards through the mass (or *vice versâ* when petroleum spirit is used); the fluid dissolves out the oil, and runs away at the exit either direct to the distilling apparatus, or to another similar cylinder where it dissolves out more oil, furnishing a stronger solution. With substances less rich in oil, such as oil-cakes, several cylinders are usually worked in succession, the fluid percolating through each, and ultimately yielding a very concentrated fatty solution, much as in the methodical lixiviation apparatus employed in dissolving crude sodium carbonate from black ash in the Leblanc soda process. The supply of bisulphide to the first cylinder is kept up until a sample of the issuing fluid is found to contain little or no oil in solution. The connection with the bisulphide supply is cut off, and then by means of a current of compressed air or of steam the fluid in the first cylinder is forced onwards into the second, which is then coupled to the supply, becoming the first of the series. The bisulphide still adherent to the exhausted material in the first cylinder is volatilised by means of steam, let in under the false bottom (or at the top), the vapours being carried to a condensing worm, where a mixture of water and bisulphide is condensed. The exhausted material is then discharged, the cylinder refilled and coupled to the series at the far end, so that the bisulphide passing in has already a considerable amount of oil in solution. In this way the nearly-exhausted material is fed with fresh bisulphide, whilst the newly-refilled cylinder is supplied with comparatively strong solution; the liquid ultimately passing out is conducted to a distilling apparatus, where the volatile bisulphide is evaporated off, and the residual fat finally collected.

Fig. 74 (*Schädler*) illustrates a set of four steam-jacketed cylinders thus used in series. A_1, A_2, A_3, A_4, are the four vessels so connected by pipes D_1, D_2, D_3, D_4, that the liquid passing off at the top of each is supplied to the bottom of the next, A_1 being reckoned next to A_4. These connections are opened and closed as required by means of the cocks E_1, E_2, E_3, E_4; H_1, H_2, H_3, H_4 are pieces of glass tubing serving as gauges. B is the carbon bisulphide supply-pipe; by means of the two-way cocks C_1, C_2, C_3, C_4, fresh bisulphide can be supplied to any one of the four vessels as required. N is a steam pipe from which steam is blown in to any vessel by means of the cocks O_1, O_2, O_3, O_4, or into the jackets through the cocks P_1, P_2, P_3, P_4. F is the saturated carbon bisulphide main, the final solution flowing into it through the cocks G_1, G_2, G_3, G_4. J is a pipe into which the liquid contents of the cylinders can be blown off through the cocks K_1, K_2, K_3, K_4. L is a compressed air main from which air can be supplied to each cylinder by the cocks M_1, M_2, M_3, M_4.

Suppose all four vessels filled with material to be exhausted; by opening the cock C_1, connection is established between the bisulphide main, B, and the cylinder A_2, through the pipe D_1, and cock E_2; bisulphide then flows into A_2, percolating through the material until the level of the cock C_2 is reached; this is set so as to shut off the bisulphide main and open the connection with A_3 through D_2 and E_3, and consequently the bisulphide passes onwards into A_3. In similar fashion it passes successively into A_4 through C_3, D_3, and E_4, and into A_1 through C_4, D_4, and E_1. Finally, it is drawn off through G_1 into the saturated solution main, F, whence it flows to the still (or an intermediate store tank). The progress of the extraction is judged by the colour visible at the gauge, H_2; when the liquor is seen to be devoid of colour, all available oil has been dissolved. The cock C_1 is then closed so as to shut off the bisulphide supply; E_2 is closed, and M_2 and K_2 opened, so that compressed air enters A_2 and forces the liquid contents out through the discharge pipe, J; the steam cocks O_2, P_2 are then opened, so that the cylinder and contents are heated, the bisulphide vapour thus produced being driven out along with some water vapour through J to a condensing apparatus. To avoid loss of bisulphide vapours not completely condensed but carried away with the escaping air, this is made to pass through an absorbing vessel containing oil which dissolves out the bisulphide, forming a liquid from which the bisulphide is recovered by distillation when strong enough.

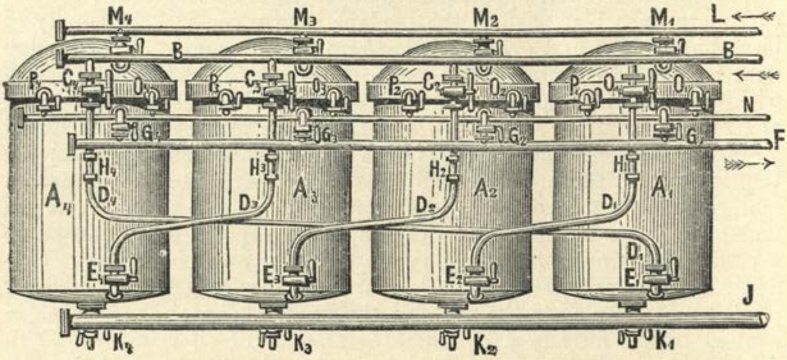

Fig. 74.—Apparatus for Oil Extraction by Solvents.

The cylinder A_2 being exhausted and all bisulphide evaporated off, the manhole is opened, the exhausted charge withdrawn, and a new one introduced. A_2 is then coupled on in front of A_1 and the whole operation recommenced, the order in which the fresh bisulphide passes through the series being now A_3, A_4, A_1, A_2, instead of A_2, A_3, A_4, A_1, as at first. In similar fashion, A_3, A_4, and A_1 are in turn exhausted and recharged.

Fig. 75 represents a Heyl's distillation apparatus for boiling off the carbon bisulphide from the fatty solution thus obtained. A is a boiler-plate vessel furnished with a steam-jacket, B, at the base. Steam is let in at C, and the condensed water drawn off at D. The bisulphide solution is supplied at E, the gauge F enabling the right level to be attained. L is the draw-off pipe for the oil finally left; J J, exit leading to condenser; H, an agitator worked by a handle, G; K, a tube through which steam can be led into a circular pipe at the base inside, perforated with a number of minute orifices. The solution being run in, steam is turned on so that boiling soon commences, the bisulphide vapours being led away through J to the condenser. The agitator, H, facilitates the evaporation; at the end steam is blown in through K, so as to pass through the residual oil in a multitude of fine streams, which drive off the last traces of bisulphide vapour. Finally, the oil is drawn off through L, and a fresh charge introduced.

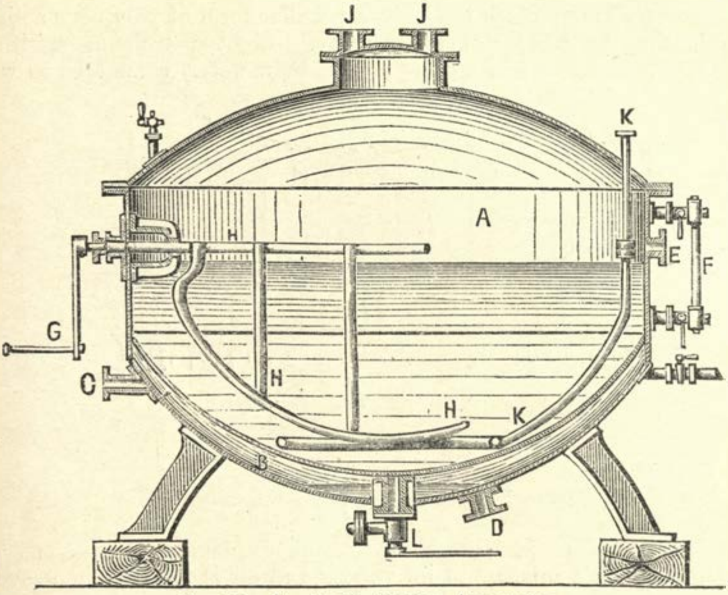

Fig. 75.—Heyl's Distillation Apparatus.

Deitz's Apparatus (Fig. 76).—Fig. 76 represents a simpler form of extraction apparatus consisting of an extraction tank, B, into the bottom of which bisulphide is pumped from the well, A, by the pipe, *h*, the fatty solution passing off at the top through the pipe, *f*, to the still, D; the vapours here evolved are led away through the pipe, *e e*, and condensed by the worm, C, the condensed bisulphide returning to the well, A. When the extraction is complete, the bisulphide supply is shut off and steam injected into B through a coil at the base below the false bottom, *d d*. The residual fluid in B is thus forced back into A, and as the heat becomes greater, the bisulphide still remaining in the exhausted mass is volatilised and carried to the worm, C, through the pipe, *e e*. The heat is supplied to the still, D, by means of a steam coil inside; finally, steam is blown through the residual oil to remove the last traces of bisulphide, and the oil drawn off through the discharge pipe, *i*. A series of these extractors is generally employed, worked in couples alternately.

Carbon bisulphide being heavier than water is comparatively readily protected from evaporation by a layer of that fluid on its surface; on the other hand, its vapour is very inflammable, and when breathed for long periods produces a peculiar form of poisonous action, culminating in a species of insanity. Light petroleum spirit is cheaper, but, owing to its being lighter than water, cannot be so well protected from evaporation and consequent danger of fire and of explosion when a mixture of its vapour and air is ignited; moreover, its solvent action is less rapid. The former solvent is more generally used in Europe, the latter in America.

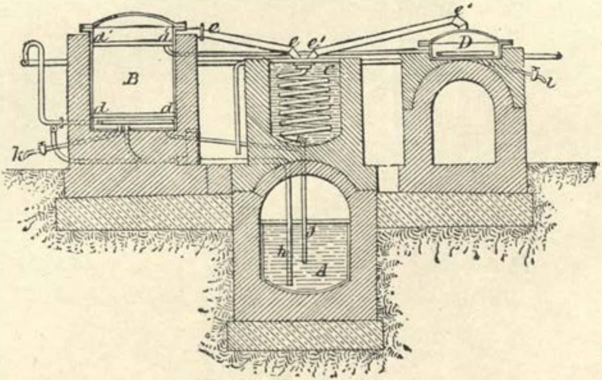

Fig. 76.—Deitz's Extraction Apparatus.

Grills and *Schroeder* have patented the use of *liquefied sulphur dioxide* at 30° to 40° C. under a pressure of some six atmospheres as a solvent for oils for extraction purposes (Eng. Pat. 19,948, Dec. 11, 1889); and *Lever* and *Scott* have similarly patented the use of *carbon tetrachloride*, which is said to yield a purer product than carbon bisulphide (Eng. Pat. 18,988, Nov. 26, 1889).

In a method of extraction patented by *Abel* (Eng. Pat. 2,360, 1900) the process is carried out under water or in closed chambers, so as to avoid any loss of solvent which in this case, too, is carbon tetrachloride.

The *Cleveland Linseed Oil Company* have patented (Eng. Pat.

Solvent.	Boiling Point. °C.	Freezing Point. C.	Specific Gravity at 25° C.	Coefficient of Expansion.	Heat of Vaporisations. Calories.	Refractive Index.	Viscosity at 25° C.	Specific Heat.
Chloroform, ...	61·5	..	1·4791	0·001257	..	1·449 (15° C.)	..	..
Carbon tetrachloride, . .	76·7	..	1·5835	0·001227	..	1·464 (15° C.)	..	..
Dichlorethylene, cis., . .	48·8	..	1·3328	0·001360	6,930	..	0·457	..
Dichlorethylene, trans., . .	59·8	..	1·3345	0·001270	7,268	..	0·510	..
Trichlorethylene, . . .	87·5	— 73	1·4542	0·001193	7,436	1·47914 (17° C.)	0·615	0·223
Tetrachlorethylene, . .	121·0	— 19	1·6080	0·001078	8,554	..	0·940	0·216
Tetrachlorethane, . . .	147·5	— 36	1·5881	0·000998	9,134	1·49559 (17° C.)	1·808	0·268
Pentachlorethane, . . .	159·1	— 22	1·6712	0·000909	8,829	..	..	0·266
Hexachlorethane, . . .	185·5 (at 776 mm.)	— 187	2·01 (?)	..	..	..	2·432	..

23,106, 1895) a process of expelling the solvent from the extracted oil by steam at a temperature not exceeding 140° F. It is claimed that in this way coagulation of albuminous substances is prevented, and the extracted linseed oil rendered as suitable for certain technical purposes as the expressed oil.

One advantage which petroleum spirit (boiling at about 110° to 115° C.) has over carbon bisulphide is that it does not attack metals.

During the last few years chlorohydrocarbons have been introduced as solvents, and, like carbon tetrachloride, are non-inflammable. On the other hand, their vapours are poisonous, and they attack iron and aluminium. The physical properties of these solvents in comparison with chloroform and carbon tetrachloride are shown in the table of *Gowing-Stopes*[1] on the preceding page.

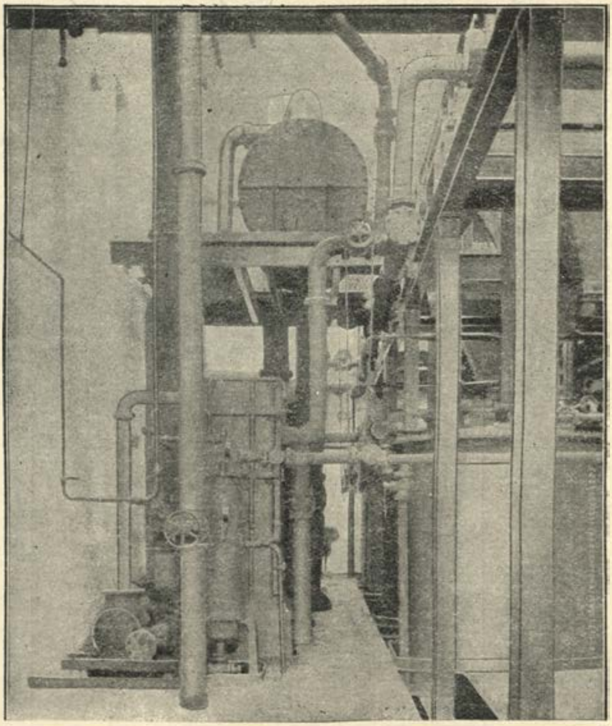

Fig. 78.—View of an Extraction Plant.

The accompanying diagram (Fig. 77) shows the cross-section of an English solvent extraction plant capable of treating 600 tons per week, and Fig. 78 represents a view of a portion of the plant.

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[1] *Analyst*, 1914, xxxix., 5.

Extraction of Grease from Engine Waste, etc.—The greasy cotton-waste, rags, etc., that accumulate where machinery is largely used from the wiping of spindles and cleansing of metal work, etc., and similar materials, are sometimes treated with solvents for the purpose of recovering the oily matter, after which the material is more or less cleansed by boiling with alkalis, etc., and washing, so as either to be capable of use over again or to be suitable for paper-making. The plant used for this purpose differs little from that above described. An old boiler or some similar vessel is erected, and provided with a false bottom or grating at the base, and suitable manholes. The solvent liquid is run in (from the base, if carbon bisulphide or tetrachloride, because those liquids become lighter by dissolving fatty matters; from the top, if light petroleum spirit, for the opposite reason), so as to percolate through the greasy rags, etc., the solution obtained being distilled so as to recover the solvent and separate the grease. Owing to the prevalent use of hydrocarbons in preparing lubricating oils, the grease thus obtained is rarely available for soap-making, except when largely admixed with other fatty materials.

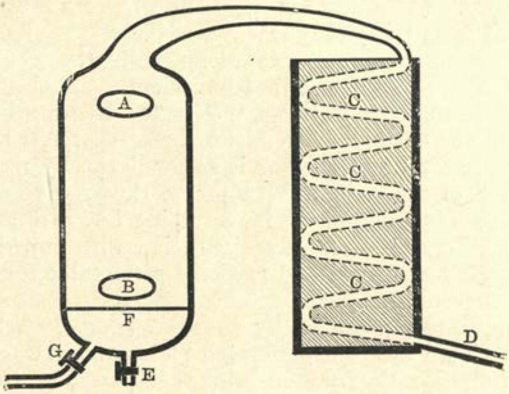

Fig. 79.—Plant for Cleansing Engine Waste.

Fig. 79 represents an arrangement used in Lancashire for the purpose of cleansing engine waste, and recovering grease therefrom. It consists of a vessel of boiler plate, about 9 feet high and 6 feet in diameter, with a grating, F, forming a false bottom, and a gooseneck leading to a worm condenser, C; G is a pipe supplying steam, and E a cock for withdrawing grease. The grating, F, is fixed about 2 feet above the bottom, and consists of a disc of ½-inch boiler plate pierced with numerous slightly conical holes, 1½ inch in diameter on the upper side, 1 inch in diameter on the under side. Some 3 tons of greasy waste are shovelled in through the upper manhole, A. Coal-tar benzene, boiling not higher than 100° C., or benzoline (light petroleum distillate) is then pumped in through A, and percolating through the mass dissolves out grease, the solution accumulating under the false bottom. A is then closed and made vapour-tight with lime paste.

Steam is then blown in through the pipe, G; the vapours evolved at first become condensed in the comparatively cool mass of waste above, and thus serve to wash out the remaining greasy solution adhering to the latter. Presently the vapours pass over into the condensing worm, C, made of 2 to 3-inch leaden or iron piping, arranged so as to form 10 to 12 turns 6 feet in diameter; a plentiful supply of cold water is admitted at the base of the cistern in which the worm is set, passing off by an overflow pipe at the top. Finally, when all volatile matters are expelled from the still, and nothing but water is condensed in the worm, the steam is shut off, and the waste extracted through the lower manhole, B. To complete the cleansing it is boiled in a kier with soda, washed plentifully with water in a dash-wheel, soaked in dilute hydrochloric acid to dissolve out oxide of iron, again washed in the dash-wheel, drained in a centrifugal machine, and hung up to dry. From 50 to 60 per cent. of cleansed waste is usually thus obtained from the greasy raw material.

The recovered benzene runs along with the condensed water through D to a covered cistern (conveniently an old boiler), where the two separate by gravitation; the lighter hydrocarbon is pumped up again into the extraction vessel for a new charge, whilst the water is run away from time to time as it accumulates, by means of a cock at the bottom of the cistern. The grease thus recovered is generally too impure to be used directly for anything but cart grease or other coarse lubricating purposes. By distillation with superheated steam, it may be partially purified and rendered serviceable for various other purposes.

In an apparatus, patented by *Heywood* (Eng. Pat. 25,228, 1900), the waste is placed between perforated plates and extracted by means of carbon bisulphide, the solution being then passed on to a still, where the solvent is distilled off and recovered.

Somewhat similar methods are in use for the extraction of "wool-fat" from raw wool (*vide Lanoline*).

Determination of Fat in Seeds, etc.

When it is required to determine analytically the amount of oils and the like present in a solid substance chiefly containing non-fatty constituents (*e.g.*, crushed seeds or oil-cake, the residue left on evaporating milk or cream, and such-like materials), the process adopted is substantially an application on the small scale of the general principles involved in the large-scale extraction methods described above. When the fatty matter predominates, the weighed portion of substance is stirred up with ether, chloroform, light petroleum spirit, carbon bisulphide, or other convenient solvent, and the whole poured into a weighed paper filter, the undissolved matters being thoroughly washed out, and examined as found necessary after drying and weighing.

When, however, the fatty constituents are in the minority, the process is slightly modified: the coarsely powdered material is placed inside a piece of glass tubing, the lower part of which is constricted and blocked with cotton wool, glass wool, or asbestos fibres, etc., so as to form a strainer; the solvent is poured into the tube, percolates slowly through the pulverised material, and passes out at the lower end (filtered clear by the cotton wool) into a vessel placed to receive it, the dissolved fatty matters being obtained in weighable form by evaporating off the solvent.

Solution of fatty matter takes place more rapidly under such circumstances if the solvent be warm; to effect this, as well as to economise labour and solvent, various devices are in use, essentially modifications of the arrangement described by Soxhlet, and generally known as "Soxhlet's extractor," Fig. 80 represents one of the earliest forms, and Fig. 81 an improved form, less fragile. The substance to be exhausted is placed in the wider tube, A (Fig. 80), the lower part of which is stopped with a loose plug of cotton wool, etc., or it is wrapped in filter paper so as to form a cylindrical package, fitting loosely into A. There is no connection between the interior of B and A except through the side pipe, C. The lower end of B is made to pass through a perforated cork fitted into a weighed flask; the upper end of A is similarly connected with a reflux condenser, such as that of Allihns (Fig. 82) or a Liebig's cooler. A suitable quantity of solvent is placed in the flask, and on heating this (by means of a water-bath, etc.) the liquid is vaporised, and passes upwards through B and C to the condenser. The condensed fluid drops down into A on to the substance to be exhausted, and when the fatty solution accumulates to the lever, *h*, the siphon, D D D, begins to act, and draws off the fluid into the flask. After some 20 or 30 siphonings, all trace of fatty matter is, as a rule, dissolved out; by disconnecting the flask, and evaporating off the remaining solvent,

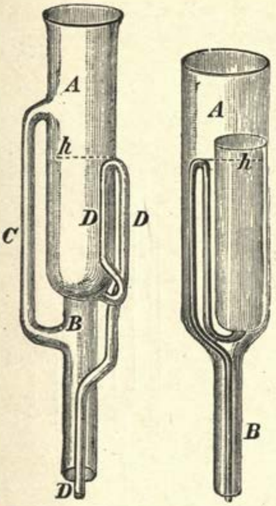

Fig. 80. Fig. 81.

Figs. 80 and 81.—Two Forms of Soxhlet Tubes.

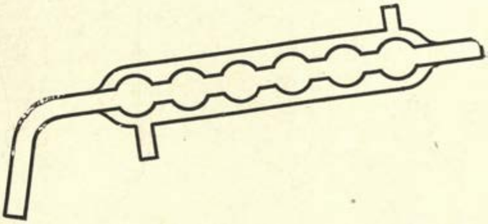

Fig. 82.—Allihns' Reflux Condenser.

the dissolved oil is obtained. In this way the solution is effected by means of solvent appreciably warmed by contact with the hot vapour in the upper part of A, whilst the operation goes on automatically.

Figs. 83 and 84 represent an improved form of Soxhlet extractor, arranged by *Frühling*.[1] The substance to be examined is placed in the vessel A (Fig. 83), provided with an internal siphon; this, when weighed, is placed inside the Soxhlet reservoir (Fig. 84) connected at the top with the lower end of the reflux condenser, C, and at the

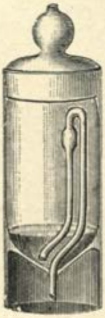

Fig. 83.

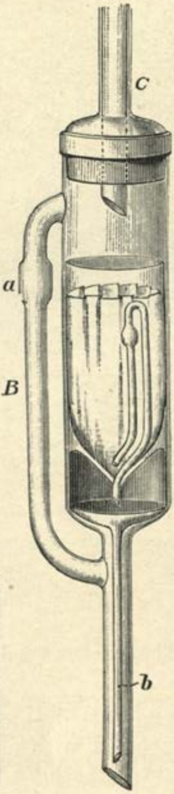

Fig. 84.

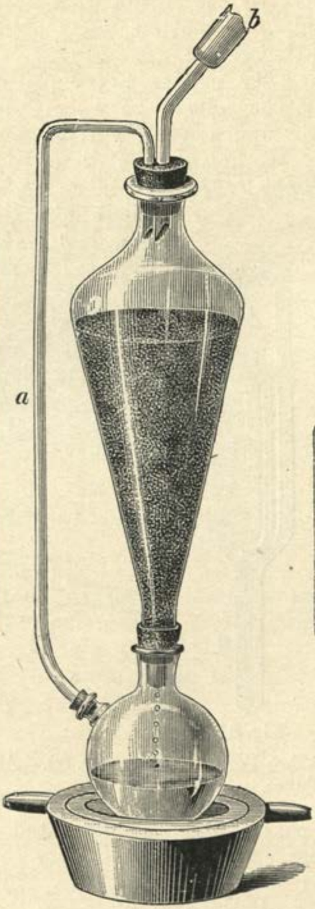

Fig. 85.

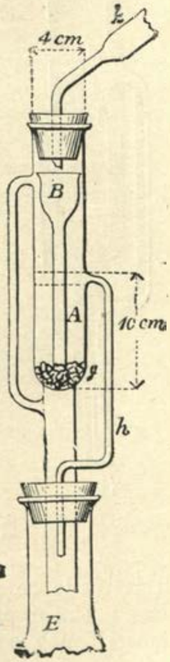

Fig. 86.

Fig. 83.—Frühling's Form of Soxhlet Tube.
Fig. 84.—Reservoir for Frühling's Soxhlet Tube.
Fig. 85.—Laboratory Extraction Apparatus.
Fig. 86.—Honig and Spitz's Apparatus.

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[1] *Zeit. angew. Chem.*, 1889, 242.

bottom, *b*, with the flask for receiving the fatty solution. The weight of substance left after removal of oil can thus be determined by simply re-weighing A.

Many other forms of extraction apparatus have been devised and recommended by various chemists for the quantitative determination of butter fat in milk residues, and such like purposes.

Fig. 85 represents a convenient arrangement on the principle of Soxhlet's extractor for the laboratory extraction of oleaginous matter from somewhat larger quantities of material.

Fig. 86 represents a modification useful for extracting unsaponifiable matters from liquids—*e.g.*, the alcoholic soap solutions obtained by saponifying oils with alcoholic alkali. The liquid is placed in the extraction vessel, A, which contains a number of glass beads; the condensed solvent (petroleum spirit) drops into the funnel, B, rises up between the beads, washing out soluble matters from the liquid, and overflows into the distillation flask, E, down the side tube, *h*.[1]

Some kinds of seeds contain a notable proportion of substances soluble in ether, other than fatty matters—*e.g.*, phytosterol and lecithin (or a mixture of lecithins); the latter, containing phosphorus, may be estimated by determining the quantity of that element contained in the ethereal extract (p. 171).

Grimme[2] has made comparative determinations of the amounts of fat extracted by means of various chlorohydrocarbons and ether, and obtained the following average percentage results:—

Ether	$CHCl_3$	CCl_4	$C_2H_2Cl_2$	C_2HCl_3	C_2Cl_4	$C_2H_2Cl_4$	C_2HCl_6
7·45	8·58	7·43	8·13	7·46	7·79	7·71	9·62

Only in the case of carbon tetrachloride and trichlorethylene are the results in agreement with those obtained with ether.

The fat in cotton-seed was not completely removed with less than 100 c.c. of either cold solvent, but forty-five minutes' extraction was sufficient with carbon tetrachloride and thirty minutes' with trichlorethylene.

In the case of substances containing less than 10 per cent. of fat the weight of residue may be accepted as sufficiently accurate, but an addition of 0·2 per cent. should be made for amounts between 10 and 15 per cent., and of 0·4 per cent. for amounts between 15 and 20 per cent. *Grimme* found that a preliminary drying of the material was not necessary.

On the other hand, *Gowing-Stopes*[3] considers it advisable to dry the substance before extraction with cold trichlorethylene, so as to obviate the formation of hydrochloric acid, which would act upon the fat.

For the physical properties of these solvents see p. 319.

The following table is abbreviated from a larger one given by *Schädler*, representing the usual proportions of total oily or fatty matter yielded by seeds, nuts, etc., of various kinds on extraction by solvents:—

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[1] Honig and Spitz, *J. Soc. Chem. Ind.*, 1891, x., 1039; from *Zeit. angew. Chem.*, 1891, 565.

[2] *Chem. Rev. Fett Ind.*, 1912, xix., 191.

[3] *Analyst*, 1914, xxxix., 4.

Name of Oil, &c.	Botanical Name of Plant.	Native Country.	Percentage Yield of Oil.
Almond,	Amygdalus communis, L.	Mediterranean.	48-50
Arachis, earth-nut, pea-nut, or ground-nut,	Arachis hypogæa, L.	India, Western Africa.	43-45 (50)
Areca-nut (cabbage palm),	Areca catechu, L.	East Indies.	14-16
Belladonna seeds,	Atropa belladonna, L.	Europe.	27-28
Bassia fat (Illipé butter),	Bassia butyracea ; B. latifolia ; B. longifolia ; B. Parkii.	Himalaya and East Indies.	49-55
Brazil-nut,	Bertholletia excelsa, Humb.	South America.	66-67
Beech-nut,	Fagus sylvatica, L.	Europe.	Shelled, 43-45 Unshelled, 27-29
Ben,	Moringa pterygosperma.	India, Egypt.	35-36
Cacao butter,	Theobroma cacao, L.	Central America.	44-47
Cameline seed (German sesamé),	Camelina sativa, L.	Europe.	31-34
Castor,	Ricinus communis, L.	East Indies.	American, 46-49 Indian, 51-53
Coconut,	Cocos nucifera, L.	Tropics.	40-45
Colocynth (Bitter apple),	Citrullus colocynthidis, L.	India, Arabia.	18-20
Colza (rape),	Brassica campestris ; B. napus ; B. rapa ; B. napobrassica, L.	Europe.	33-43
Cotton-seed,	Gossypium herbaceum, L.	Asia, Africa, America.	24-26
Croton,	Croton tiglium, L.	East Indies.	Shelled, 53-56
Cucumber-seed,	Cucumis sativus, L.	East Indies.	25-26
Cress-seed,	Lepidium sativum, L.	Europe.	23-25
Calabar bean (Poon-seed),	Calophyllum calaba, Wild.	Antilles, India.	60-65
Cashew-nuts,	Anacardium occidentale, L.	West Indies, Brazil.	40-45
Charlock-seed,	Sinapis arvensis, L.	Europe.	31-33
Candle-nuts (Bankul-nuts),	Aleurites moluccana, Wild.	Southsea Islands.	62-64
Crabwood-nuts (Carapa nuts),	Carapa guyanensīs, Aubl.	Guina, Brazil.	65-70
Centaury,	Centaurea sonchifolia, L.	Western Europe.	27-28
Chironji,	Buchanania latifolia, W.A.	Malabar.	40-45
Combo-nuts,	Myristica gabonensis, Aubr.	West Africa.	60-64
Chaulmoogra,	Gynocardia odorata, R.Br.	East Indies.	30-32
Corn-poppy,	Papaver rheas, L.	Europe.	61-65
Castanha-nuts,	Telfairia pedata, Hook.	Africa, Madagascar.	43-35
Chinese tallow,	Stillingia sebifera, Juss.	China, Punjab.	37-39
Curcas oil,	Curcas purgans, Endl.	West Indies, S. America.	Shelled, 55-57

Name of Oil, &c.	Botanical Name of Plant.	Native Country.	Percentage Yield of Oil.
Dika fat,	Mangifera gabonensis, Aubr.	West Africa.	60-64
Fever-nuts (Borneo tallow),	Hopea splendida; H. macrophylla, Vris.	Sunda Island.	45-50
Galam butter (Shea butter),	Bassia Parkii, D.C.	Tropical West Africa.	49-52
Gamboge,	Garcinia pictoria, Roxb.	India.	24-25
Grape-seed,	Vitis vinifera, L.	Asia.	11-12
Goa butter (Kokum fat),	Garcinia indica, Chois.	East Indies.	22-25
Hazel-nut,	Corylus avellana, L.	Europe.	50-60
Hemp-seed.	Cannabis sativa, L.	Asia.	30-35
Hickory-nut,	Carya amara, C. alba, Mich.	North America.	29-30
Henbane-seed,	Hyoscyamus niger, L.	Europe.	35-37
Horned poppy-seed,	Glaucium luteum. L.	Middle Europe.	30-35
Horse chestnut,	Æsculus hippocastanum, L.	Persia, India.	6- 8
Holly seed,	Ilex aquifolium, L.	Europe.	25-27
Indian butter (Fulwa butter),	Bassia butyracea, Roxb.	Himalaya.	50-52
Indian cress-seed,	Tropœolum majus, L.	South America.	46-50
Java almond,	Bursera paniculata, Lam.	Molucca.	40-42
Japan wax.	Rhus succedanea, L.	China, Japan.	22-24
Karanja butter (Ponga butter),	Pongamia glabra, Vent.	India.	34-36
Lallemantia,	Lallemantia iberica, Fisch. and M.	Persia and Kurdistan.	29-30
Lettuce-seed,	Lactuca oleifera, L.	Europe.	37-38
Laurel butter,	Laurus nobilis, L.	South Europe.	24-26
Linseed,	Linum usitatissimum, L.	The East.	38-40
Linden-seed,	Tilia macrophylla, L.	Europe.	25-28
Mahwa butter (Illipé butter),	Bassia latifolia, Roxb.	East Indies.	50-55
Maize,	Zea mais, L.	America.	6-10
Macaja butter,	Cocos aculeata, Jaqu.	Brazil, West Indies.	60-65
Madia,	Madia sativa, Molin.	Chili.	32-33
Mafura tallow,	Mafureira oleifera, Best.	Mosambique.	60-65
Mustard-seed (white),	Sinapis alba, L.	Europe.	25-26
,, (black),	Sinapis nigra, L.	Europe.	31-33
Nettle-seeds,	Urtica dioica, L.	Europe.	30-32
Nut (walnut),	Juglans regia, L.	Persia, Himalaya.	63-65
Nutmeg,	Myristica moschata, Thunb.	Molucca.	38-40
Niger (Ramtil),	Guizotia oleifera, D.C.	Abyssinia, India.	40-45
Nightshade-seed,	Atropa belladonna, L.	Europe.	27-28

Name of Oil, &c.	Botanical Name of Plant.	Native Country.	Percentage Yield of Oil.
Olive,	Olea europæa, L	Southern Europe,	Pericarp, 40-60 Kernels, 12-15
Otoba,	Myristica otoba, Humb. and B.	Columbia.	35-40
Ocuba wax,	Myristica ocuba, Humb. and B.	Brazil.	20-25
Peach-kernel,	Prunus persica. Benth.	Persia.	46-48
Palm,	Elais guineensis, Jaqu.	West Africa.	Pericarp, 65-72
	E. melanococca, Gaert.	South America.	Kernels, 45-50
Poppy-seed,	Papaver somniferum, L.	Asia Minor.	Blue, 48-50 White, 41-45
Pumpkin-seed,	Cucurbita pepo, L.	The East.	20-25
Piney tallow (Malabar tallow),	Vateria indica, L.	East Indies.	...
Pistachio-nut,	Pistacia vera, L.	South Europe.	51-53
Radish-seed,	Raphanus sativus oleiferus, L.	China.	45-50
Red-pine-seed,	Pinus abies, L.	Europe.	25-30
Safflower-seed,	Carthamus tinctorius, L.	Egypt, India.	30-32
Scotch fir-seeds,	Pinus sylvestris, L.	North Europe.	28-30
Sesamé (gingelly),	Sesamum indicum; S. orientale, L.	India, Levant, Antilles, &c.	50-57
Spurge,	Euphorbia lathyris, L.	South Europe.	43-46
Soap-berry,	Sapindus emarginatus, Roxb.	India.	30-32
Sierra Leona butter,	Pendadesma butyracea, Don.	Sierra Leone.	59-62
Sunflower-seed,	Helianthus annuus, L.	Mexico, Peru.	21-22
Spindle-nut,	Euonymus europæus, L.	Middle Europe.	44-45
Stramonium-seeds,	Datura stramonium, L.	Europe.	25-27
Spruce fir-seeds,	Pinus picea, L.	Europe.	32-33
Sapucaja-nuts,	Lecythis ollaria, L.	Brazil, Guina.	40-43
Spring poppy-seed,	Argemone mexicana, L.	Mexico, West Indies.	25-30
Tangkallak fat,	Cylicodaphne sebifera, Bl.	Java.	40 45
Tea-seeds,	Camellia oleifera, Ab.	China.	43-45
Tobacco-seed,	Nicotiana tabacum; N. rustica, L.	America.	38-40
Thistle,	Onopordon acanthium, L.	Europe.	30-35
Ungnadia,	Ungnadia speciosa, Endl.	Mexico.	9-10
Weld-seed,	Reseda luteola.	Middle Europe.	30-32
Water-melon-seed,	Cucurbita citrullus, Wgt.	Africa.	30-32
Wild radish-seed,	Raphanus raphanistrum, L.	Europe.	35-40

CHAPTER X.

ANIMAL FATTY TISSUE: EXTRACTION OF OILS AND FATS THEREFROM.

THE "adipose tissue" (ordinarily known as "fat") of the higher animals varies considerably in consistence in different cases, but uniformly consists of a cellular or honeycomb-like structure of nitrogenous non-fatty matter, the interstices of which are more or less filled with the true non-nitrogenous fatty material; hence mechanical or chemical processes are required to separate the two, just as in the case of vegetable oil-containing seeds, etc.

In some cases the melting point of the animal fat or oil is so low that processes of expression are applicable at the ordinary temperature, as in the case of certain fish livers (cod-liver oil, etc.); either the fresh organ being used, or livers that have been stored until partial decomposition has set in, more or less rupturing the oil cells. In other cases, the temperature requires to be raised in order that the fatty matter may become sufficiently fluid to exude, as in the "rendering" of tallow and lard; for this purpose the adipose tissue may either be subjected alone to heat, or may be steamed or boiled with water at the ordinary pressure or in digesters, or may be treated with hot or cold solvents for the fat, or with substances acting chemically on the nitrogenous matter of the cell-walls, and thus tending to liberate the fat.

When the nitrogenous matter is to be saved in a solid form for manure-making, the manufacture of dog-biscuit, pig feeding, or other purposes according to its quality, the first method may be employed, care being taken to prevent burning by overheating if free fire is used; or the fatty tissue may be heated in a closed vessel by means of steam and a minimum of water; or it may be finely minced and placed on sloping trays in a chamber heated by steam, so that the fatty matter gradually runs away from the solid nitrogenous cellular tissue.

If, on the other hand, the saving of the nitrogenous matter in the solid form is of no consequence, the comminuted fat may be heated for some time with water in a digester under 4 or 5 atmospheres' pressure; by this means a considerable proportion of the nitrogenous tissue is gelatinised and dissolved as a sort of glue, utilised either as such or in the manufacture of manure. In extracting fat from bones this process is generally employed; on the other hand, when the carcases of slaughtered horses, etc., are treated, long-continued boiling in open pans under ordinary pressure is more usually adopted, the fat being skimmed off from time to time as it rises. Sometimes a small quantity of soda, or of sulphuric acid, is added to the water with which rough fats are boiled, with the object of attacking the cell walls, and liberating the fatty matter more rapidly. A certain amount of loss by saponification takes place when soda is thus used (unless the impure soap formed is collected and utilised); whilst hydrolysis of glycerides is apt to be brought about by the action of acid, so that the resulting fat contains free fatty acids interfering with its use for certain purposes—*e.g.*, the manufacture of some kinds of lubricants.

In the Mège-Mouries process for preparing oleomargarine of best quality (*vide* Chap. XIV.), a sort of artificial digestion of the nitrogenous matter is brought about, chopped suet being warmed with minced sheep's stomach and a little potassium carbonate, so as to peptonise the albuminoids of the tissue and liberate the fatty matter; a much purer product is thus obtained, owing to the comparatively low temperature employed (about 45° C.) than is possible with any boiling process.

Rendering of Fatty Tissues by Dry Fusion.—When rough fats from the ox, sheep, pig, etc., are finely minced and gently heated, the melted grease gradually runs away from the solid cellular tissue. In the manufacture of butter substitutes (margarine) finely-chopped beef suet is sometimes thus heated to a temperature only just sufficient to partially fuse the fatty matter, and the runnings subsequently treated so as to separate the mass into a solid stearine, and a buttery mass largely consisting of olein. Owing to the low temperature employed (50° to 55° C.), noxious vapours are not evolved at all during the process, especially as none but the freshest fatty matter is used, any admixture of slightly tainted material greatly depreciating the value of the product.

When higher temperatures (above 100° C.) are used, the rough fats being heated over a free fire with continual stirring, the moisture present is evaporated, and the nitrogenous tissue gradually dries up and shrivels; the oil cells are thus ruptured, and the melted fat escapes. The heat usually causes a considerable amount of decomposition of the tissue, leading to the evolution of most atrocious smells, especially if the fatty tissue is stale, tainted, or partly decomposed. By straining off the melted fat, and pressing the residual "greaves" or "cracklings," in such a press as is shown in Figs. 41, 45, 46, the majority of the fat present is extracted; if the cracklings are intended as food (for dogs or pigs) the presence of a little residual fat therein is an improvement rather than otherwise; if required, a further amount of grease can be extracted by boiling with dilute sulphuric acid, or heating in a pressure vessel, so as partly to gelatinise the solid animal matter and liberate the remaining fat.

An improved dry heat rendering arrangement has been patented by *Merryweather & Sons*, in which the materials to be rendered are placed in a steam-jacketed pan, into the jacket of which superheated steam is passed, so that the danger of "burning" the fat is greatly lessened, whilst the heat can be much more easily regulated; accidents from fire through the pan contents suddenly foaming over can be minimised, whilst fuel is economised, and the wear and tear of the pan lessened.

The blubbers of the seal, of the whale, dugong, porpoise, and other cetacea, and the livers of the shark, cod, dog-fish, kulp, and other fish, are generally allowed to remain in baskets or other perforated vessels at the ordinary temperature for some time, so that a first running of purer oil may be obtained spontaneously; later on, heat is applied to facilitate the extraction. Formerly "boiling down" whale blubber for train oil was an operation performed on the whaling vessel shortly after the capture of the animal; at the present day the blubber is more frequently brought ashore (either to port or to fishing stations for the purpose) for treatment. A certain amount of oil is generally collected by the simple process of placing the cut-up mass in racks, from which the oil drips gradually into casks; later on decomposition commences, and the oil then exuding is inferior in quality. Finally, the remaining mass is "boiled"—*i.e.*, subjected to dry heat to extract the remaining oil. In some cases wet steam heating (*infra*) is applied at first, whereby the process is much shortened.

In order to mitigate the nuisance arising from the emanation of foul-smelling vapours during the dry process for rendering fats, etc., various contrivances have been tried from time to time, such as passing the evolved vapours through layers of charcoal or through scrubbers containing alkaline or acid solutions, etc.; the only really effective method, however, depends on the destruction by combustion of the malodorous emanations, the fumes and vapours evolved being collected by a hood or pipe and made to traverse the fireplace of one of the works' boilers; or otherwise similarly consumed. Preferably the vessels are enclosed in a sort of casing, so that the vapours evolved are led away by means of a pipe to the spot where they are consumed, an indraught being maintained by means of a fan or steam jet.

Rendering of Fatty Tissues by Heating with Water or Steam under Ordinary Atmospheric Pressure.—The extraction of fatty matter from adipose tissue is often greatly facilitated by finely mincing the tissue, or crushing it between rollers, and then placing it in a pan with water, the temperature of which can be raised as required, either by injecting wet steam, employing a dry steam coil or steam jacket, or by means of free fire, etc. For the preparation of oleomargarine, a process of this description is often used as the first stage, selected fresh fat of highest quality being chosen, and the temperature being kept as low as possible, consistent with the melting out of the more fusible constituents, which rise to the top and are skimmed off. Latterly, a higher temperature is used whereby a more solid fat (when cold) is obtained; and, finally, the heat is raised to 100° C. to extract the last portions of fatty matter. This, however, is rarely completely effected unless either a higher temperature (under pressure) is applied, so as largely to gelatinise the nitrogenous tissue, or sulphuric acid is added so as to break up the fat cells by its solvent action on the nitrogenous matter. In the extraction of fat from bones boiling in open pans for some twenty-four hours, simple water is often employed, the bones being broken up into lumps so as to expose the fat cells as much as possible. The fat is skimmed off as it rises, and the liquor utilised for the preparation of size; a larger yield of fat, however, is obtained when high-pressure vessels are employed (*vide infra*).

Fish Oils.—Various fish oils are extracted by similar processes. Thus, in the preparation of cod-liver oil, the fresh healthy livers are first placed in open barrels, so that a certain proportion of oil spontaneously exudes; after a while they are transferred to metal pans, heated gluepot fashion in a larger external hot-water vessel, or by a steam jacket; here a further separation of oil ensues, of second quality. Finally, the livers are boiled with water, when a still lower grade separates. The quality of the second runnings varies according to the temperature employed in the first heating. When 40° to 50° C. is not exceeded, a much finer oil is obtained than when 75° to 80° C. is reached, more nearly approximating to the first runnings ("cold drawn" oil), but possessing a more marked brownish-yellow tinge. Oil extracted by boiling with water is usually of a more or less deep brown hue.

According to *P. Möller*, of Christiania (Eng. Pat. 13,803, 1890), the fishy unpleasant flavour of cod-liver oil is largely due to the absorption of oxygen during its extraction, and may consequently be to a considerable extent avoided by rendering the livers in vessels from which all atmospheric air is excluded by means of a current of indifferent gas, such as hydrogen or carbon dioxide.

In order to prevent fermentation, *Schuseil* (Eng. Pat. 4,594, 1899) wraps the liver in sacking, wire gauze, or the like, before expressing it.

Several species of fish of the herring and sardine class are employed in different countries as sources of oil, the simplest method of procedure adopted being to slice and mash the fish, and pour boiling water over the mass, which is then stored in barrels, etc., for some time; decomposition sets in, and the fat tissues become disintegrated, so that the oil floats up and is skimmed off at intervals. A more systematic method, adopted in the case of menhaden oil and other fish oils extracted by means of modernised appliances, consists of thoroughly boiling or steaming the fish (whole and unbroken, or sliced and mashed), and then subjecting it to comparatively gentle pressure. The first runnings thus obtained are considerably superior to the second grade, prepared by boiling or steaming the residue a second time, and pressing again with stronger pressure and at a higher temperature; the screw press heated by steam, shown in Fig. 45, is well adapted for this process. The ultimate residue is utilised for manure: after being squeezed as dry as possible, preferably by hydraulic pressure, the residual solid mass is broken up and allowed to ferment, dried somewhat, ground and sifted, and finally dried further, so as to form a powder convenient for transport. Large quantities of fish manure are thus prepared from the residues of the extraction of oil from the "menhaden" or "porgie" at numerous places along the North American Atlantic coast.

D'Arcet's Sulphuric Acid Process for rendering tallow consists in melting the adipose tissue with from one-fifth to half its weight of water, and a few per cents. of sulphuric acid, keeping the entire mass boiling until the separation of fat is completed, the heat being applied by means of a free fire, by a steam jacket, or by directly blowing in steam; in the latter case, somewhat less water is originally added, with a proportionate increase in sulphuric acid strength, to compensate for dilution by condensation of steam. When this method is adopted, the vessel may be simply constructed by lining a cask or tank with sheet lead; whereas, for boiling over free fire, a copper vessel must be employed, iron being too readily attacked by the acid.

In *Evrard's* process, the sulphuric acid is replaced by caustic soda; the evolution of fœtid smells is thereby lessened, but loss is apt to be occasioned through the formation of soap by the action of the soda on the fat.

According to a patent of *Stanley and the Fish Utilisation Syndicate* (Eng. Pat. 7,269, 1896) the fatty material is boiled with water containing a suitable proportion of sodium silicate, and the oil subsequently washed with water until free from alkali. This treatment is said to break open the fat-containing cells, and also to effect some deodorisation and purification.

When rough fats are rendered in a soapery for use therein, a simple method is to place the tissues to be treated in one of the soap "kettles" or "coppers" (Chap. XIX.), and blow wet steam through the mass; a large proportion of the fatty matter is then melted down, and is removed by skimming. To extract the remainder, weak alkaline lyes from other operations are run in, and the whole boiled up with steam so as to convert the fat into a kind of impure soap solution, which is run off and worked up together with other inferior material in the manufacture of lower grades of scouring soaps.

When partly decomposed tissues, etc., are boiled to extract fat, much the same kinds of noxious smells are apt to be evolved, as in the dry process (p. 330). Accordingly, when it is essential to avoid nuisance, it is usual to box in the pans, and lead the evolved vapours to a condensing chamber where the steam is condensed, the remaining air, etc., being drawn off to the main chimney-stalk of the works, by which means a continuous indraught is set up, and outward leakage of malodorous vapours avoided. In the case of putrid materials, the mere dilution of noxious vapours with the chimney gases thus brought about is not always sufficient, and destruction of smell by fire must be resorted to in order to avoid nuisance in certain situations, such as crowded towns, and the like.

Treatment of Fish Offal.—*Wymonde's* digester (Eng. Pat. 22,916, 1898) consists of an upright cylinder through which passes a shaft bearing specially arranged blades. The fish is introduced at the top and treated with high-pressure steam while continually turned over by the blades. The expressed oil falls through a perforated false bottom, and the residual matter is forced through a special door by reversing the agitator blades.

Rendering under Increased Pressure.—Of all processes for obtaining fats from their natural animal sources this one is the most extensively used, as the higher temperature attained leads to the more complete gelatinisation of nitrogenous tissue, and consequently to the more thorough separation of fat. Fig. 87 represents a digester employed in Wilson's process for rendering tallow and lard; a series of these is generally worked together, each of 10,000 or 15,000 gallons capacity, or even more. In large American slaughter-houses (*e.g.*, at Chicago,

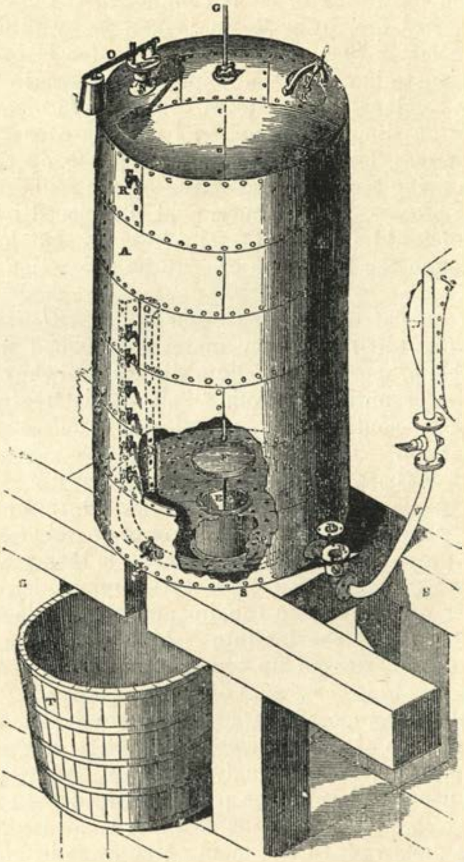

Fig. 87.—Wilson's Digester.

St. Louis, Cincinnati, etc.), each digester is kept for the production of one kind of fatty matter only, the adipose tissue being usually worked up within a few minutes after slaughtering; hence injury through use of stale or decomposed fatty tissue is avoided, and extremely uniform grades of lard and tallow obtained, the various portions of the carcases being separately treated in different vessels according to the part of the body employed.

The boiler is provided with a false bottom; a discharging orifice, E, covered when required by a plate, F, raised or lowered as required by the rod, G, passing through a stuffing-box; an internal steam coil at the base fed with steam from an ordinary boiler by the pipe, V, and steam cock, B; and a series of draw-off cocks at the side, U, *p*, *p*, *p*, *p*, R. A safety valve, O, is also provided, and a manhole at the top, K.

The discharging valve being closed by lowering F, the fat to be rendered is introduced through the manhole, K, until within 2 to 2½ feet of the top; the manhole being closed, steam is admitted through the cock, B, until the desired pressure is obtained (usually 3 to 4 atmospheres). Much water condenses during the heating up; if required this is drawn off from time to time by means of the lowest cock, U, the progress of the fusion being tested and regulated by opening the top cock, R, so as to see whether only steam escapes, or melted fat. After ten to fifteen hours the steam supply is shut off and the excess pressure relieved by opening the safety valve; the whole is then allowed to remain at rest awhile so that the fatty matter and water may separate, when the former is drawn off into coolers through the side cocks, *p*, *p*, *p*, *p*, and the latter through the lowest cock, U. The aqueous liquor contains much nitrogenous matter in solution and is utilised in the manufacture of manure. The solid contents are finally discharged from the boiler by raising the valve, F; the substances ejected are collected in a tub, T, and if not completely freed from fat are returned to the boiler and worked over again with the next charge.

Davidson has patented a process (Eng. Pat. 25,472, 1896) of treating the adipose tissue of cattle with steam under pressure and separating the fat from the resulting fluid mass by means of centrifugal force.

Extraction of Fat from Bones.—Before bones are treated for the preparation of manure, animal charcoal, etc., the fatty matters which they contain are usually more or less completely extracted by one or other of a variety of processes. Of these the simplest consists in boiling the bones (preferably crushed into coarse fragments) with water heated by a steam jet or otherwise; the fatty matters are thus melted out and separated by skimming them off as they rise to the top of the water.

A large fraction of the total fatty matter is thus left behind in the osseous tissue through incomplete removal. A better yield, however, is obtained when the heating is effected under increased pressure in a digester, the steam then penetrating into the minute cavities and more completely displacing the melted fat. Moreover, the nitrogenous cell wall constituents are usually gelatinised to a greater extent than is effected by open pan boiling, so as to facilitate the escape of fat. For this same reason, however, the bones thus treated are rendered poorer in organic constituents, and, therefore, less suitable as manure or for animal charcoal making; on the other hand, more soluble organic matter, suitable for glue making or for manure, etc., passes into the watery liquor.

Digesters.—Various forms of digester are in use. A useful variety consists of a vertical wrought-iron barrel or cylinder some 6 feet long and 3 feet 6 inches in diameter, slightly tapered at each end, and fitted with flanges to which iron discs can be bolted (Fig. 88). The upper plate, *b*, serves as lid, so that when removed fresh bones can be introduced; the lower one, *c*, is slightly curved; when removed the boiled bones are discharged.

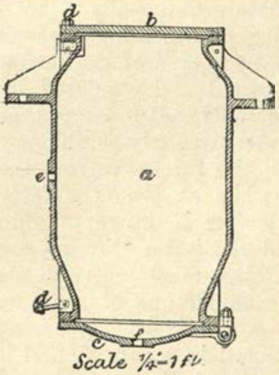

Fig. 88.—Barrel Digester for Extracting Fat from Bones

A charge of 2 to 2½ tons of crushed bones being introduced, the plates are bolted on steam-tight, the operation being facilitated by fastening the plates on with hinges, so that they are virtually doors. Steam at 3½ to 4 atmospheres' pressure (56 to 65 lbs.) is then introduced for about three-quarters of an hour. When shut off the pressure is relieved, and the whole allowed to stand for half an hour, after which the condensed water and melted fat are drawn off through a tap, *f*, in the bottom plate or door. This door is then opened and the exhausted bones removed, after which a fresh charge is introduced and worked off as before.

Even when operating in this way a certain amount of fatty matter is still left in the bones. To avoid this, in some Continental factories solvents are used (carbon bisulphide, benzene, light petroleum distillate, etc.), the mode of treatment being very much the same as that adopted for the similar extraction of grease from vegetable *marc*, engine waste, etc. (*vide supra*); the crushed bones being placed in suitable vessels into which the solvent is run, preferably traversing several in succession, and the fatty solution being subsequently distilled to recover the solvent and obtain the grease.

Owing to the peculiar texture of bone as compared with vegetable seeds, even this mode of treatment does not produce a perfect solution and removal of all the fatty matters present. In order to obtain a larger yield, various modifications of the plant have been introduced, whereby the solvents are made to act on the crushed bones in the form of vapour. In one form of apparatus, this is effected under increased pressure (after pumping out all atmospheric air from the vessel employed), so that the solvent enters thoroughly into the pores of the bone fragments, and being attracted to and condensed by the fatty matters, forms a fluid solution of fat which exudes and runs down to the bottom, and is subsequently distilled (Seltsam's process).

In another form the crushed bones are permeated with a mixture of steam and vapour of solvent, which is condensed by a worm so as to drop down again upon the bones and percolate through them to a false bottom, where the solvent is again volatilised by a steam coil, the whole arrangement being not unlike that used for cleansing engine waste (Fig. 79).

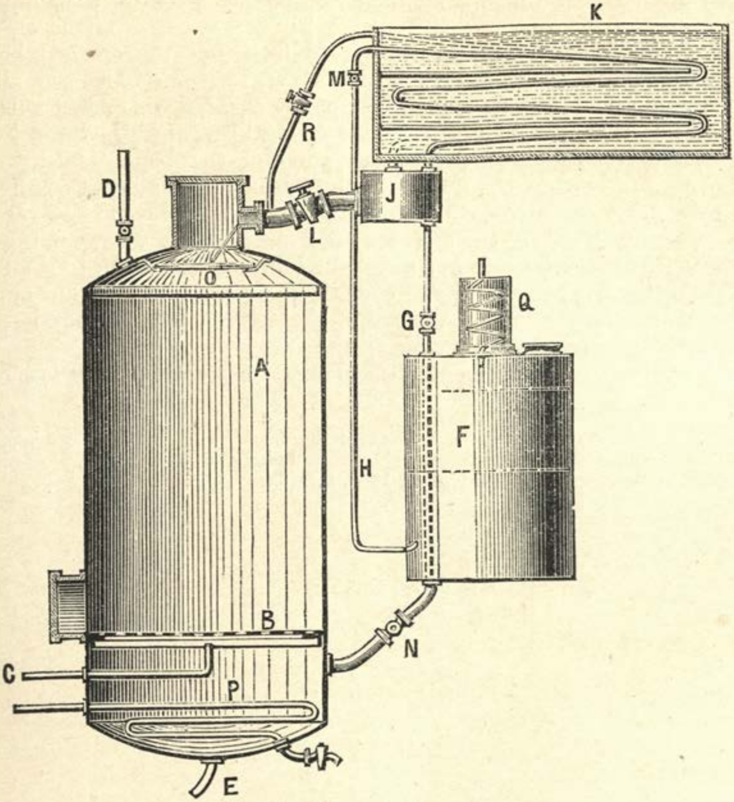

Fig. 89.—Leuner's Apparatus.

Fig. 89 represents Leuner's apparatus arranged on this principle (*Schädler*). The crushed bones are placed in A above the perforated false bottom, B. C is a steam pipe, by means of which the bones are steamed as a preliminary, the surplus steam escaping through the exit pipe, D. After steaming, water and benzene are run in from the reservoir, F, into the space under the false bottom, and heated up by the steam coil, P. The evolved vapours are condensed in the worm, K, and at first run back over the bones through the cock, L, the vapour passing upwards to the worm through J, and the condensed liquid being divided into separate streams by the spreading plate, O. After some time the cock, G, is opened, so that the condensed liquid runs into the reservoir, F, instead of flowing back into A. When all the solvent has been volatilised, nothing but water condenses in the worm, which is known by means of a sampling cock attached to J′; the draw-off cock, E, is then opened, and the watery gelatine solution and oily matter run off into a suitable separating receptacle; A is then discharged through a manhole and refilled, and the whole operation repeated.

Another method of operating is to introduce the crushed bones into a sufficiently strong false-bottomed vessel, from which the air is then pumped. Benzene, carbon bisulphide, or other convenient volatile solvent is then run in until the vessel is filled, whereby the solvent fluid is driven thoroughly into the pores of the bone tissues. By drawing off most of the fluid and then again exhausting, the solvent is to a great extent volatilised; and by re-admitting air the vapour is again condensed by the increased pressure so as to wash out the fat solution from the bone fragments. The solution runs down to the base of the vessel, and is ultimately distilled by working the air pump, leaving the fat, while the vapour of the solvent pumped out is condensed by cooling and used over again.[1]

The arrangement of an English plant for extracting bones is shown in Fig. 90.

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[1] For further details of bone-fat extracting plant *vide* Schädler, *Technologie der Fette und Oele*, 2nd Edition, edited by Lohmann, 928, *et seq.* Also for Seltsam's process, *J. Soc. Chem. Ind.*, 1882, i., 112.

CHAPTER XI.

REFINING AND BLEACHING ANIMAL AND VEGETABLE OILS AND FATS, WAXES, ETC.

SUSPENDED SUBSTANCES.

OILS and fats as obtained by many of the processes in ordinary use contain various impurities partly in suspension, partly in solution. Of these the most objectionable are the gummy mucilaginous or albuminous matters which generally accompany expressed oils and rendered fats to a greater or less extent, because unless speedily removed they are apt to undergo fermentative or putrefactive changes, which not only induce hydrolysis of the glycerides, but also charge the oil with malodorous bye-products of decomposition, rendering the oil "rancid."

Substances of this kind are, as a rule, chiefly in suspension in the oil; so that by passing the freshly-expressed oil through a filter-press, a considerable proportion of the suspended matter is removed, rendering the oil in many cases sufficiently clear and free from visible impurities to be at once saleable. Sometimes, however, the suspended matter is present in a form where filtration alone produces only an insufficient amount of purification, and where even prolonged standing does not efficiently clarify the oil by subsidence. This happens more especially when the mucilaginous matter is disseminated throughout the oil in a sort of highly diluted jelly-like condition, somewhat analogous to colloidal gelatine or thin starch paste, where the constituent particles are, for the most part, too fine to be stopped by means of ordinary porous filtering media, or to gravitate rapidly.

In such cases recourse must be had to special mechanical or chemical treatment in order to coagulate the mucilaginous matter.

Heat.—Sometimes simply heating the oil produces this effect, the albuminous substances being solidified and coagulated somewhat like white of egg. This is conveniently effected by blowing steam through the oil by means of a fine rose jet; the condensation of water facilitates the action as the coagulated albuminous matter attracts moisture and becomes increased in bulk and deposits more readily as a flocculent precipitate on standing.

In an apparatus designed by *Rocca* (Eng. Pat. 10,899, 1900) the oil passes through a series of chambers arranged as in a column-still, and meets a current of steam, which is introduced at the bottom and bubbles successively through each chamber.

Addition of Chemicals.—The addition of small quantities of various chemicals often produces an analogous effect; thus a small percentage of sulphuric acid, or of concentrated zinc chloride solution (sp. gr. 1·85), well agitated with the oil causes on standing the gradual deposition of mucilage, along with most of the acid, the rest being subsequently removed by agitation with water. Oils containing resinous matter (*e.g.*, cotton-seed oil) as well as mucilage are preferably refined by similar treatment with alkalis, the resin being thereby dissolved out and removed as well as vegetable mucus.

Morgan's Hydro-refiner.—In *Morgan's* process (Eng. Pat. 19,806, 1900) cold water in a fine state of division is forced through the oil under a pressure of about 18 feet. The resulting semi-emulsion is left at a temperature of 20° to 25° C. until the water separates, drawing down with it the insoluble impurities.

The *hydro-refiner* used for this purpose has a cylinder which is open at the top and provided with an outlet at the bottom. The water issues under pressure from holes in a central tube and breaks up the oil on its passage through the cylinder.

Mechanical Attraction.—The purely physical action exerted by particles of suspended matter as regards attracting the colloidal mucilage often serves to remove the latter. Thus clay, fuller's earth, sand, particles of oil-cake, powdered charcoal, and similar materials, when well agitated with the oil or melted fat under treatment, tend to unite with the mucilage, in such fashion that by allowing the whole to subside, or by filtering it, the whole of the suspended matter is simultaneously separated.[1]

In certain cases the addition of chemicals that combine with the albuminous matter to form precipitates answers the same purpose; thus oak-bark infusion and other forms of tannin solution, when well agitated with the oil, cause the formation of insoluble tanno-gelatinous matter which precipitates on standing, carrying down with it most of the colloidal suspended matter. Various metallic salts (copper sulphate, manganese sulphate, lead acetate, etc.) are sometimes used with a similar object.

The same principle underlies *Linde's* process for purifying rapeseed and other sweet oils (Eng. Pat. 13,201, 1900). The oil is heated with 10 to 15 per cent. of milk at a temperature not exceeding 100° C., and filtered from the sediment carried down by the coagulated proteids in the milk.

A process of this kind sometimes used for cleansing rancid tallow is to boil the material with a small quantity of soda lye; the melted fat is removed from the soap produced by ladling off, and then boiled

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[1] In many cases a very satisfactory degree of purification is readily effected by simply adding to the mucilaginous oil, as it runs from the press, a small quantity of cake parings ground up by edgestones, and then passing the whole through a filter-press; the residue left in the filter-press is returned to the kettle and worked up with fresh crushed seed, etc. Still better clarification may often be effected by heating the mixture of oil and parings, so as to coagulate albuminous matter, and then passing through the filter-press.

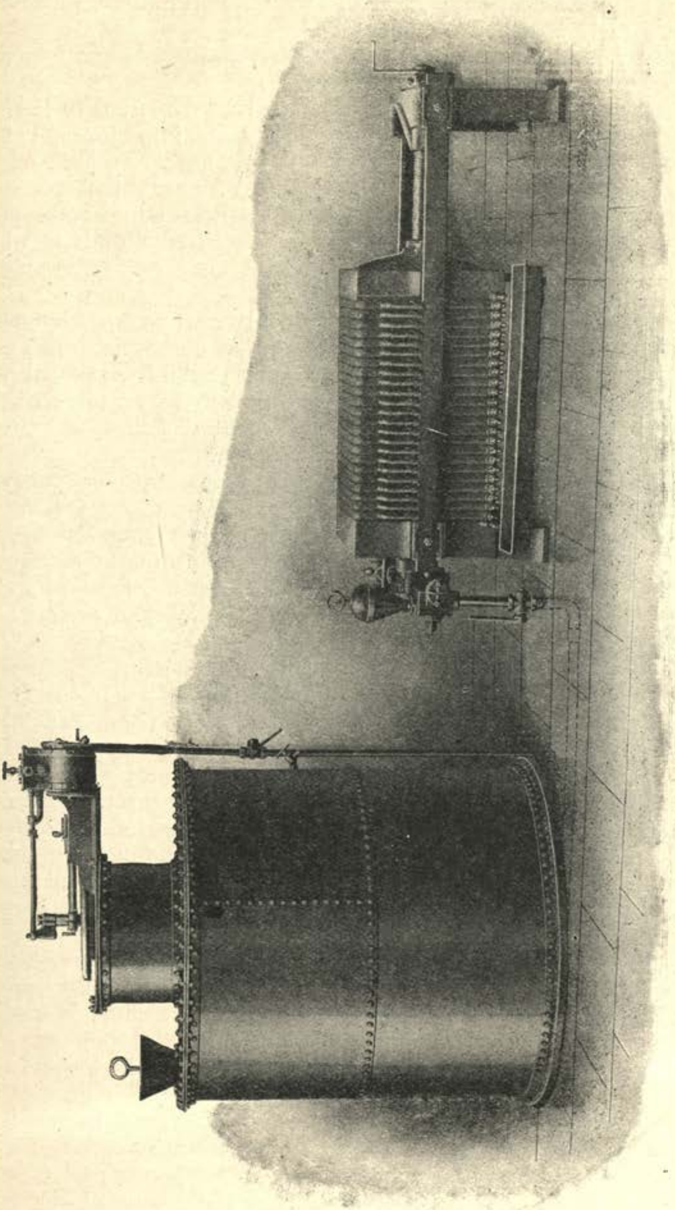

Fig. 91.—Plant for Treatment of Oils and Fats with Fuller's Earth.

up with a weak solution of alum; after settling, the purified tallow is again run off and heated by itself to 150° C. and upwards, whereby it becomes greatly whitened and hardened.[1]

Fig. 91 represents a view of a plant for treating oils and fats with fuller's earth.

The oil or fat to be treated is previously heated to 150° to 180° F., the temperature being a matter of considerable importance, and is meanwhile stirred by the mechanical agitating gear. As soon as the temperature has again been brought to 150° F. from 3 to 5 per cent. of absolutely dry and finely powdered fuller's earth is added and rapidly mixed by means of the agitator. In the case of edible oils to which the fuller's earth may impart an unpleasant taste, it is advisable to effect the treatment at a lower temperature.

After the admixture the contents of the mixer are pumped by means of a steam pumping engine into the filter-press, into which dry steam is admitted during the expression, so as to expel the oil from the cakes.

When viscid oils, such as linseed, and especially castor oil, are being treated, the temperature of the room in which the filtration is done should be at least 90° F.

Methods of Filtration.—Many forms of apparatus for purifying oils by filtration have been devised.

For example, in *M'Clelland* and *Jackson's* process (Eng. Pat. 24,080, 1894) the oil is introduced into a vessel at the top of the apparatus, and passes through a strainer into a bell beneath a column of water, whence it rises through a layer of filtering material, and is drawn off from the surface of the water.

A similar process of forcing the oil upwards through filtering material, and then water, is claimed by *Brooks* (Eng. Pat. 14,441, 1895).

An oil filter patented by *Richmond* and *Crowther* (Eng. Pat. 2,160, 1898) consists of a cylindrical casing divided by means of a plate into an upper and lower portion. Through the plate is suspended a small cylinder containing filtering material, surrounded by a second cylinder also containing filtering material, whilst a third perforated cylinder is placed over both. When oil is introduced into the upper compartment the heavier impurities settle on the plate while the oil passes through the filters.

Several processes of centrifugal filtration are also in use.

Fisher's oil filter (Eng. Pat. 7,265, 1899) has a siphon arrangement for drawing off the clearer oil from subsiding impurities, whilst upward filtration, assisted by the production of a partial vacuum, is used in an apparatus patented by *Beckmann* (Eng. Pat. 3,608, 1900).

Dissolved Matters.—Other impurities are dissolved in the oil, and the complete separation of these is in many cases impracticable. Resinous matters are the commonest impurities found in solution; these are generally of a feebly acid character, so that agitation with small proportions of alkaline solution removes the larger part or even the whole of these. For this purpose soda, potash, milk of lime, and

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[1] *Oil Trade Review*, Oct. 1884.

calcined magnesia are employed in different instances; carbonated alkalis and alkaline earths (carbonate of soda, lime, etc.) usually act only imperfectly. When the proportion of resin is at all large the saponaceous compound formed sometimes separates only with difficulty from the clarified oil; agitation with saline solutions (sulphate of soda, or common salt, etc.) in such cases generally causes the mass to separate into three layers on standing; the lowest one a watery fluid containing chiefly inorganic salts in solution; the uppermost, clarified oil; intermediately, a more or less frothy mass of "foots." Frequently this contains so much unaltered oil mechanically entangled as to be highly valuable material for soap-making, the resinous soap also present usually not interfering with this application.

Purification of Bone-Fat.—Bone-fat extracted by boiling-processes generally retains in solution calcium phosphate and other calcium salts to an extent greatly interfering with the preparation of soap from this material. Boiling with dilute sulphuric or hydrochloric acid converts the lime into calcium sulphate or chloride, and completely removes these inorganic dissolved impurities, the operation being very simply performed by placing the fat in a tank lined with sheet lead, together with a sufficient quantity of highly diluted acid, and blowing wet steam through the mass so as to agitate it thoroughly. Sulphuric acid has the advantage of cheapness and of acting less on the lead than hydrochloric acid; on the other hand, insoluble calcium sulphate forms and is deposited, whereas calcium chloride, being readily soluble, does not separate in the solid form.

Separation of "Stearine."—Certain oils when chilled deposit the less readily fusible constituents as "stearines." On subjecting these to filtration and pressure, an oleine practically free from suspended albuminous matters generally results, any such impurities being for the most part retained along with the stearine. A partial separation of stearine by allowing the oil to stand at a relatively low temperature, is accordingly sometimes resorted to as a means of clarifying and refining oils, more especially the more expensive edible oils ("salad" oils); the thickened mass being pressed in a filter while chilled, or on the small scale being strained through rough filters of moss, cotton wool, charcoal, etc., placed between the perforated bottoms of two boxes, one just fitting inside the other. Oils that have been thus treated are sometimes termed "winter oils"—*i.e.*, oils still remaining fluid in winter; whilst untreated oils that become turbid or partially solidify on chilling and are only clear in warm situations are designated "summer oils."

In a process devised by *Adams* (Eng. Pat. 6,753, 1900) for the purification of linseed oil, the albuminous substances are first coagulated by heat and then separated by means of filtration or centrifugal force. The oil is next chilled so as to cause the deposition of stearine, etc., and again filtered. An apparatus for carrying out these processes continuously is also described in the same patent.

Unsaponifiable Matter.—Even after as complete a removal as possible of suspended albuminous and mucilaginous matter and of dissolved resin, most natural oils and fats contain in solution small quantities of non-saponifiable non-resinous matters. In some cases cholesterol or its isomerides (iso-cholesterol, phytosterol, etc.) have been identified—*e.g.*, in olive oil. The following figures are given by *Allen* and *Thomson*[1] and *Schädler*[2] as representative in various cases:—

Oil or Fat.	Percentage of Unsaponifiable Matter.	
	Allen & Thomson.	Schädler.
Cotton-seed oil,	1·64	1·85
Coconut oil,	...	0·80
Hemp-seed oil,	...	1·00
Japan wax,	1·14	1·20
Cod-liver oil (brown),	1·32	1·45
,, ,, (light).	0·46	0·50
Linseed oil,	...	1·10
Almond oil,	...	0·45
Poppy-seed oil,	...	1·15
Olive-oil (yellow),	0·75	0·80
,, (green),	...	1·50
Palm butter,	...	1·25
Rape-seed oil (crude)	1·00	1·30
,, ,, (refined),	...	0·15
Hog's lard,	0·23	0·30
Tallow,	...	0·50

The following figures were obtained by *Thomson* and *Ballantyne*[3] in the course of an extended examination of numerous samples of oils:—

Name of Oil.	Percentage of Unsaponifiable Matter.
Olive oil (13 kinds),	1·04-1·42
Cotton-seed oil (crude),	1·12
,, ,, (refined),	1·07
Rape oil (colza, 5 kinds),	0·58-0·70
Arachis oil,	0·54-0·94
Linseed oil (4 kinds),	1·06-1·28
Castor oil,	0·30-0·37
Southern sperm oil,	37·41
Arctic sperm oil (bottlenose),	36·32
Whale oil (pale),	1·82
Seal oil (4 kinds),	0·42-0·51
Cod oil (3 kinds),	0·87-1·87
Menhaden,	1·60

In the analysis of soap (Chap. XXII.), as the unsaponifiable substances originally contained in the fatty matters employed for the

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[1] *Chemical News*, xliii., 267.

[2] *Technologie der Fette und Oele*, 61.

[3] *J. Soc. Chem. Ind.*, 1891, x., 233.

most part pass into the soap during manufacture, a correction on this score is necessary when it is desired to determine the mean equivalent of the fatty acids present. According to the author (*Alder Wright's*) experience the amount of matters of unsaponifiable nature thus contained in 100 parts of fatty acids, etc., separable from the soap by means of a mineral acid, generally lies between 0·25 and 1·0 part, averaging about 0·5 to 0·75—*i.e.*, in the case of soaps made from natural oils and fats, to which no additional unsaponifiable matters have been intentionally added. When wool-grease or Yorkshire grease (Chap. XII.) has been used, either purposely as an ingredient, or unwittingly in the form of an adulteration of tallow, etc., the proportion becomes markedly increased. With olein soaps made from distilled olein a few per cents. of hydrocarbons are often present, formed during the distillation of the fatty acids, smaller quantities being often found in soaps made from oleins prepared in the autoclave without distillation. When paraffin oils have been intermixed with the soap, as in the case of certain kinds of laundry soaps, the percentage of unsaponifiable matters is largely increased.

The fatty matters extracted by solvents from certain leguminous plant seeds (peas, lupins, etc.) contain relatively considerable proportions of glycerophosphoric derivatives of the nature of lecithin (*q.v.*); the existence of small quantities of substances of this class in oils expressed for commercial purposes is extremely probable, but little is known as to how far this is the case. The husk of the seeds of *Lupinus lutrus* yields to either a crystallisable substance, *lupeol*, analogous to cholesterol, but derived from a hydrocarbon poorer in hydrogen; whilst the seed husks of *Phaseolus vulgaris* contain a higher homologue of phenol (viz., *phasol*, $C_{15}H_{24}O$) together with paraphytosterol. In all probability several such substances akin to cholesterol and phytosterol are contained in small quantities in seed oils.

SULPHURIC ACID PROCESS FOR REFINING OILS, ETC. (THÉNARD PROCESS).

In employing sulphuric acid as a clarifying agent it is essential that no large excess should be used, since otherwise a charring action is apt to affect the oil itself, darkening its colour and depreciating its value. In refining linseed oil from one-hundredth to one-fiftieth part (1 to 2 per cent.) of acid[1] is thoroughly intermixed with the oil in an efficient agitator at a temperature not exceeding 40° C. (about 104° F.), and the whole allowed to rest for twenty-four hours. 60 to 70 per cent. of warm water at about 60° C. (140° F.) is then well intermixed, and the whole allowed to stand some days; a watery acid liquid separates at the bottom with a layer of flocculent "foots" above which is the clarified oil, which is drawn off and again agitated with warm water as before to wash out any residual suspended acid vesicles.

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[1] Hartley recommends that the acid should be diluted with water before mixing with the oil, so as not to contain more than 30 per cent. of actual H_2SO_4.

Another method of operating (*Cogan's* process) is to use 1 per cent. of acid diluted with as much more of water; this is well intermixed, and after standing some hours is heated up to 100° C. by blowing in steam through a fine rose jet at the bottom of a copper vessel. This temperature in maintained for several hours, after which the whole is allowed to stand at rest so as to separate the watery acid and foots from the clear oil. In order to draw off the oil without disturbing the water and foots, a conical separating vessel is generally employed with taps at various levels, so that all clear oil above a given level can be drawn off without disturbing that below.

Rape (colza) and linseed oils and certain fish oils are those most usually refined by the acid process. Oils intended for lubrication are as a rule the least suitable for such treatment, inasmuch as the presence of free fatty acids in quantity (and *a fortiori* of possible traces of mineral acids) is a serious objection with most such substances, corrosion of bearings and shafts, etc., being apt to be thereby occasioned. For oils intended for burning in lamps the presence of any considerable amount of free fatty acids is also objectionable as tending to cause charring of the wick.

Zinc Chloride.—*R. v. Wagner* recommends the use of zinc chloride solution of specific gravity 1·85 instead of sulphuric acid, using about 1½ parts per 100 of oil. Albuminous impurities are equally destroyed or coagulated, whilst there is less danger of injurious action on the oil itself. *Hartley* finds that a strong solution of manganese sulphate answers well.

Liquid Sulphur Dioxide.—For the purification of oils for illuminating or lubricating purposes *Villon*[1] uses from 0·5 to 1 per cent. of liquid sulphur dioxide. The reagent is introduced in a tube into the oil, which is contained in a boiler lined with lead, and its action accelerated by heat. When cold the oil is thoroughly washed with warm water and filtered. By treating the oil with zinc chloride before the addition of the sulphur dioxide still more satisfactory results are said to be obtained.

ALKALINE REFINING PROCESSES.

As already stated, processes where alkalis are used as agents for coagulating and removing mucus, albuminoids, etc., have several advantages over the acid methods, notably that free fatty acids and resins are also removed. The quantity and strength of the alkaline lye employed vary with the nature of the oil to be treated; any undue excess is apt to lead to more or less considerable loss, not only by producing more saponification but also because the extra amount of saponaceous products gives rise to the formation of more foots containing clarified oil entangled therein. The requisite quantity of lye and the oil are well agitated together by any suitable mechanical mixer (either in the cold or heated to the necessary temperature, as

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[1] *J. Soc. Chem. Ind.*, 1895, xiv., 665.

the case may require), and the whole then allowed to settle. A heavier watery fluid with soapy foots separates; this is drawn off and the process repeated with a much weaker alkaline solution, and subsequently with plain water.

When considerable quantities of resin are present, as in the case of cotton-seed oil, the lye may conveniently be of specific gravity 1·06 up to 1·10; in such cases it frequently happens that the watery layer and foots will not separate thoroughly from the oil without the subsequent addition of a little salt or brine.

To avoid the formation of emulsions Hageman employs as purifying agent soda crystals heated to about 80° C. so as to fuse in their water of crystallisation. After intermixture by agitation the mass separates on standing into three sharply-defined layers of purified oil, soapy matters, and watery fluid respectively, but without any notable production of emulsion.

Sodium Peroxide.—*Burton* (Eng. Pat. 963, 1900) claims the use of sodium peroxide as a refining agent. The violence of the reaction is moderated by previously rendering the oil slightly acid, whilst the rapidity of the evolution of oxygen is checked by the addition of a solution of sodium phosphate.

Spermaceti.—Crude spermaceti is generally refined by processes partly involving the mechanical expression of fluid oil, somewhat after the fashion of stearine pressing (p. 343), and partly of a chemical nature, more especially boiling up with a small quantity of potash lye. This dissolves out free fatty acid formed by the hydrolysis of the cetin or otherwise, and saponifies most of the residual fluid oil, this being more readily acted upon by alkalies than cetyl palmitate itself. Simultaneously, however, some of the latter becomes saponified, and in consequence the foots contain more or less considerable amounts of potassium palmitate, etc., whilst the purified spermaceti contains an admixture of cetylic alcohol.

Utilisation of "Foots."—The foots obtained from oils containing considerable quantities of resinous matter (*e.g.*, cotton-seed oil foots) are sometimes directly worked up into soap by admixture with other materials in the soap boiling process. When their colour or nature prevents this being done, they are generally acidified so as to decompose the soaps present. The mixture of fatty and resinous acids and more or less undecomposed glycerides thus obtained is usually distilled by means of superheated steam, whereby the glycerides present are hydrolysed; the fatty acids distil, whilst the resinous matters mostly remain behind as a pitchy mass. To some extent, however, the materials are generally broken up by the heat with the formation of high-boiling hydrocarbons and water, the former of which partly distil with the fatty acids. The result of this is that "distilled oleins" obtained from products of this kind will not wholly dissolve in alkaline solutions to soaps, the hydrocarbons remaining undissolved. On agitating the liquid with an appropriate volatile solvent (ether, petroleum spirit, etc.) a quantity of unsaponifiable matter can usually be dissolved out from the soap solution to the amount of several per cents. of the distilled olein employed. The same remarks apply *a fortiori* to the analogous products obtained when "Yorkshire grease" (Chap. XII.), wool-grease, and similar materials are distilled by means of superheated steam.

The appliances used for such distillation with superheated steam consist essentially of a boiler for steam raising; a superheater whereby the steam is heated considerably above the temperature of the boiler generally consisting of a coil of iron tubing heated in a flue or some analogous arrangement; a distilling vessel into which the material to be distilled is run, the steam being then blown through it in numerous fine streams by means of a rose jet at the bottom, or a coil perforated with small holes; and a condensing apparatus in which the evolved vapours and the steam are condensed. In Chap. XVII. the arrangements employed in the candle material manufacture for the distillation of fatty acids and glycerol by means of superheated steam are described; those used for the distillation of foots, recovered greases, etc., do not greatly differ from these.

It often happens that the solidity of a grease, etc., is greatly increased by the process of distillation with superheated steam, so that a comparatively soft grease after distillation gives a product of much stiffer consistence, and capable of yielding a considerable amount of solid "stearine" by pressure. The cause of this is not absolutely certain; but it is extremely probable that it is due to the conversion of oleic acid into isomerides of higher melting point, iso-oleic acid, or stearolactone, or both (p. 45); just as these products are formed by the action of zinc chloride on oleic acid (p. 203), or during the decomposition of glycerides by sulphuric acid and their subsequent distillation with superheated steam in the "Wilson" process for obtaining candle material (Chap. XVII.).

Precipitation Processes.—In some few cases oils and fats contain mucilaginous or albuminous matters not readily removable by mechanical means alone, such as subsidence or filtration, but readily coagulated by means of certain metallic compounds or substances containing tannin.

Thus in "boiling" linseed oil to improve its drying qualities (Chap. XIV.) sulphate of zinc, acetate of lead, sulphate of manganese, and other metallic salts are sometimes used, not only for the purpose of facilitating the incipient oxidation and physical alteration required to make the oil dry to a varnish more rapidly, but also in order to combine with, and remove by subsidence, the last portions of vegetable mucilage, etc., not entirely removed by previous refining operations.

Some kinds of fish oils are similarly improved by vigorous agitation with oak-bark infusion or other liquors, containing tannin, conveniently effected by blowing a rapid current of steam through the whole: gelatin is thus precipitated and removed by deposition on standing, any excess of tannin taken up by the oil being subsequently removed by agitation with lead solution or other appropriate metallic salt.

Copper sulphate solution, alone or mixed with brine, when thoroughly intermixed with fish oils, may often be used effectively for removing gelatin, etc., therefrom by precipitating it as an insoluble compound.

H. Nordlinger has patented (German Pat. 58,959) a process for refining vegetable oils and precipitating mucilaginous matter consisting of the preparation of " purification-oils " by dissolving in from 10 to 20 parts of oil the zinc, cadmium, iron, manganese, lead or copper salts of the higher fatty acids (metallic soaps), at a temperature of about 150° C., and allowing the liquid to clarify by subsidence. From 5 to 10 per cent. of the metallic soap solution thus prepared are then added to the oil to be treated and the whole allowed to stand some time, when precipitates are formed by the interaction on one another of the mucilaginous matter and the metallic compounds; the clear supernatant purified oil is drawn off when the action is complete.

Hartley and *Blenkinsop* patented (Eng. Pat. 11,629, 1890) the use for refining linseed oil of a solution of manganese linoleate in oil of turpentine or other suitable solvent: 1 part of manganese salt to 800 of oil suffices. If much mucilage is present the oil is previously treated with sulphuric acid of 30 per cent. By blowing a current of air or oxygen through the mass at a temperature of about 190° F. (88° C.), bleaching is readily effected, the manganese salt acting as a carrier of oxygen.

De la Roche (Eng. Pat. 26,539, 1898) treats the cold oil with calcium carbide, and allows the sediment containing the water and mucilaginous matters to settle, the clear oil being subsequently separated by decantation or filtration. It is claimed that linseed oil thus treated is rendered brilliant, and that its drying properties are greatly improved.

BLEACHING OILS AND FATS.

The colours exhibited by certain oils and fats, as obtained from their respective sources, are in general due to the presence of natural organic colouring matters (xanthophyll, erythrophyll, chlorophyll, etc.) in solution in the oil; in some cases these are mostly mechanically carried down by the mucilaginous matter present during clarification by subsidence, etc., more especially when heat is also applied to promote the coagulation of albuminous impurities, and particularly when oak-bark or other sources of tannin are employed as precipitants of these bodies; in some instances albumin or gelatin is purposely added with tannin, to precipitate the colour. Some colouring matters are removable by treatment with animal charcoal and filtration somewhat after the fashion of sugar refining; exposure to a moderately high temperature destroys others; whilst in yet other cases chemical bleaching agents are necessary, such as oxidation by the action of air blown through the heated oil, either alone or in presence of oxygen carriers; or chlorination by means of small quantities of bleaching powder or chlorate with hydrochloric acid; or both together by means of potassium dichromate and dilute hydrochloric acid.

With high-priced substances such as beeswax, bleaching by exposure to air and light in thin cakes or ribbons, and in some cases treatment with nitric acid or peroxide of hydrogen, is applicable, although the cost of labour and chemicals is prohibitive of such methods in the case of the cheaper oils, etc. On the other hand, reducing agents, such as ferrous sulphate or sulphurous acid, answer better than oxidising ones with some kinds of oils—*e.g.*, linseed oil.

For the decolorisation of palm oil *Garle* and *Frye* (Eng. Pat. 26,682, 1896) employ a current of ozone, ozonised air, or ozonised oxygen at a temperature not exceeding 100° C.

Steam-Jacketed Oil Mixer.—Fig. 91*a* represents a form of apparatus manufactured by W. Neill & Son, Ltd., for mixing oils, etc., for bleaching. It is constructed of steel plates, and has a steam jacket extending from the bottom half-way up the sides. The agitator, which works in the lower part of the vessel is an archimedean screw, and is driven by reversible gear. This screw, working in an interior cylinder, raises and lowers the oil, thereby causing intimate admixture of the whole of the contents of the vessel. The apparatus here shown is capable of dealing with a charge of 10 tons, but it is also made in larger sizes.

Hot Air Process.—Certain fats, especially tallow and palm butter, can be pretty thoroughly decolorised by heating them and passing a current of air through the dry mass (containing no interspersed water) by means of a large rose with fine orifices, so that many fine streams of air bubbles rise through the hot fat. A temperature somewhat short of that of boiling water generally suffices (80° to 90° C.). In the case of palm oil a somewhat higher temperature, 125° to 130° C.,[1] also effects the destruction of the colouring matter in the absence of air; a considerable amount of the glyceride is thereby decomposed with evolution of acrolein, and formation of free palmitic acid.

Many fish oils are greatly lightened in colour by blowing air through the mass, heated to about 100° C. in a steam-jacketed vessel. In these cases the oil itself generally becomes more or less oxidised, increasing in density and viscidity, especially if the air-treatment be carried too far (*vide* "blown oils," Chap. XIV.). In Hartley and Blenkinsop's process for refining linseed oil (*supra*), the oxidising action of the air is intensified by adding a manganese soap which acts as a carrier of oxygen.

Instead of blowing a stream of air through the oil to be treated, *Teal* (Eng. Pat. 18,744, 1892) exposes rape-seed or linseed oil, etc., in a finely divided stream to air at a temperature of about 170° F. (71° C.), in order to "brighten" the oil.

W. Mills (Eng. Pat. 18,244, 1891) bleaches and purifies non-drying oils and fats by means of a mixture of hot air and volatilised sulphur

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[1] 240° C., according to Pohl, who first introduced the process. *Dingler's poly. J.*, cxxxv., 140.

trioxide, SO_2, passed into a " mixer " capable of withstanding a pressure of 2 atmospheres. The sulphur trioxide acts as an oxidising agent,

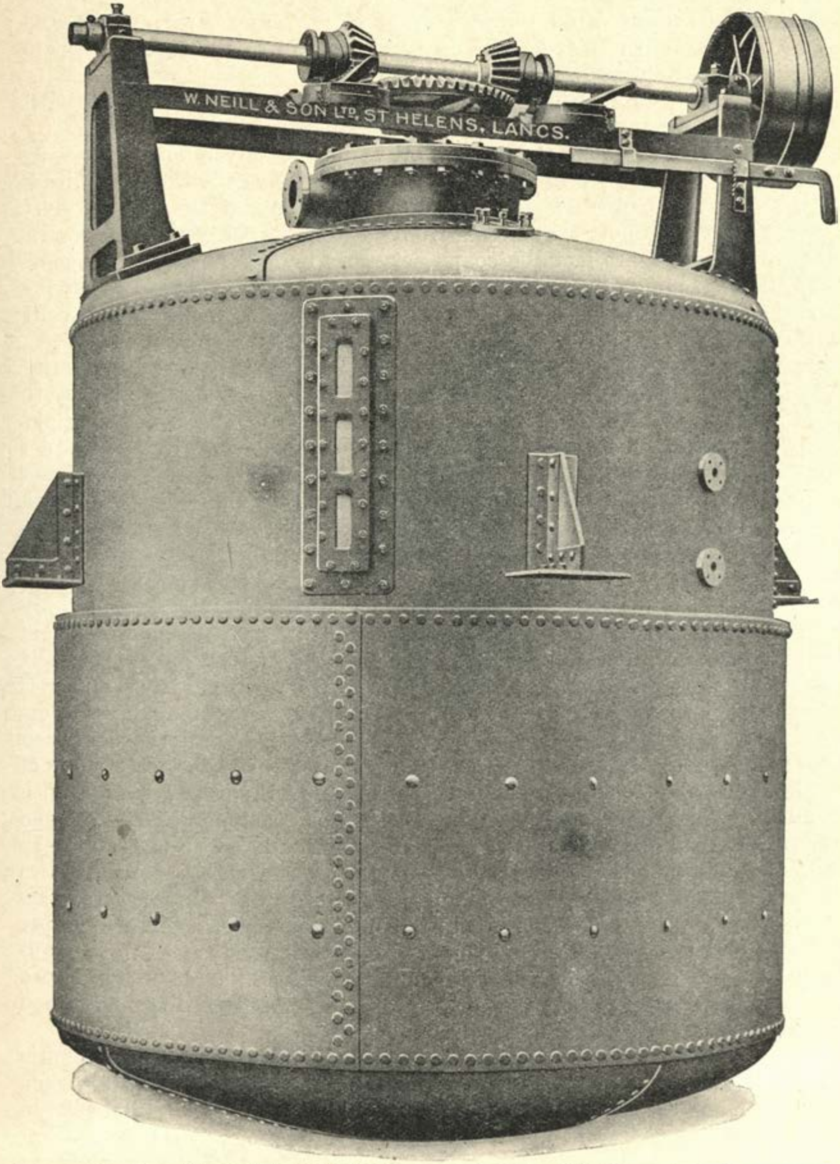

Fig. 91*a*.—Steel Jacketed Oil Mixer, with Reversible Screw Agitator.

becoming reduced to sulphur dioxide, which also is effective, especially whilst nascent.

In a process patented by *English* (Eng. Pat. 9,799, 1897) linseed oil is first subjected to a temperature of 300° F., and is then distributed by means of perforated arms on to the bottom of a chamber where it is heated to 600° F.

The bleaching action of hot air is accelerated by the presence of catalytic agents (Eng. Pat. 17,784, 1913).

Rai[1] has studied the action of various catalysts, including air-bleached palm oil, oleates of manganese, nickel, cobalt, copper, lead, and iron, in the presence of a current of air at 80° to 90° C. The catalyst was used in proportions ranging from 0·1 to 0·33 per cent. The results showed that most metallic soaps act more or less as catalytic agents in the bleaching of palm oil and tallow, but not of beeswax, so that the time required to bleach the fat is considerably shortened. Cobalt salts are the most effective agents, whilst manganese salts come next.

Dichromate Processes.—In the bleaching of raw palm oil by *Watts'* dichromate process, the oil is rendered quite fluid by heating it to 40° to 50° C., and is intermixed with 1 to 1·25 per cent. of its weight of potassium dichromate dissolved in hot water (22 to 28 lbs. per ton). Strong hydrochloric acid solution to the extent of 2 to 2·5 per cent. of the oil is then run in with vigorous agitation, enough being used to ensure that a slight excess of free acid shall finally be present in addition to that neutralised by the chromium and potassium. The reddish-orange hue changes rapidly, first to a dark brown, then to a brownish-green, and finally to a light green, the operation taking only a few minutes. The whole is then heated up by blowing wet steam through, and allowed to stand at rest for some hours; the supernatant bleached oil is drawn off and used directly for soap-making, etc., or is washed by agitation with hot water, and standing to remove traces of chrome liquor. The "green liquor" resulting from the operation is sometimes worked up to recover the chromium by adding milk of lime so as to form a precipitate of chromium hydroxide mixed with lime. This is washed and drained, and then roasted, whereby oxygen is taken up and calcium chromate formed, and this used for a fresh batch instead of potassium dichromate. When there are difficulties as to running waste chrome liquors away into water courses, etc., this method of regeneration is practically imperative; but unless a proper amount of scientific skill and supervision is exercised (not always available in a soapery), the cost of labour and fuel, etc., is apt materially to outweigh the value of the potassium dichromate saved, except when the price of this salt is unusually high.

Instead of hydrochloric acid, a mixture of two parts of sulphuric acid and three of common salt may be employed, the latter being dissolved with the dichromate, and the former gradually run in to the mass after having been diluted with about twice its bulk of water. If the temperature be too high, the bleaching is not always

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[1] *J. Soc. Chem. Ind.*, 1917, xxxvi., 948.

successful, a brownish "foxy" shade being developed about 45° to 50° C. may be taken as a working maximum; the proportion of dichromate used need not exceed 28 lbs. to the ton ($\frac{1}{80}$ part = 1·25 per cent.) in skilled hands.

A similar mode of treatment is available with many other oils, the use of hydrochloric acid to generate nascent chlorine not being necessary in all cases. Thus with various fish oils a few pounds of dichromate to the ton, with about half as much sulphuric acid, answer best, the oxidation being completed by adding a small proportion of nitric acid largely diluted, and boiling up with steam. In other instances, treatment with dichromate improves the product, not so much by simply bleaching as by oxidising and removing the small quantities of malodorous substances present that communicate a fœtid or rancid odour—*e.g.*, kitchen grease, horse grease, etc.

Beeswax is frequently bleached by being boiled with a weak solution of potassium dichromate, acidulated with sulphuric acid. The product is apt to retain chromium compounds, giving it a greenish hue; boiling up with oxalic acid solution appears to be the best mode of dissolving out the chromium and furnishing a white product. Instead of "chromic liquor," dilute nitric acid is sometimes employed, care being taken not to use too much or to have it of too great strength; otherwise more or less considerable loss is apt to occur through oxidation of the wax itself.

Wax thus bleached by oxidising chemicals is generally more crystalline than air-bleached wax, and consequently not so well suited for the manufacture of wax candles. According to *Leopold Field*,[1] whilst the solubility in alcohol of air-bleached wax differs but little from that of the raw wax, that of chemically-bleached wax is much greater, leading to the idea that free fatty acids are largely formed during the bleaching process, giving greater crystallinity.

Instead of potassium dichromate, manganese dioxide has been employed for bleaching oils, especially palm oil. The powdered substance suspended in water is intermixed with the oil by vigorous agitation, and hydrochloric acid added so as to generate chlorine, whilst the whole is heated by blowing in steam. The only advantage of the process seems to be the lessened cost, against which several other inconveniences must be set off, the action being far less regular. The same remark applies to the process formerly used to some extent where manganese dioxide and sulphuric acid were employed.

Chlorine Processes.—Chlorine evolved from substances other than potassium dichromate and hydrochloric acid is sometimes employed as a bleaching agent. Thus, tallow may be bleached by boiling it on a solution of bleaching powder or potassium chlorate to which hydrochloric or sulphuric acid is added; about 2 to 2·5 lbs. of chlorate per ton usually suffices. In all such processes, when the fat is intended for soap-making, excess of chlorine is apt to produce a worse result than none at all so far as colour is concerned (leaving deodorising out

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[1] *J. Soc. Arts*, xxxi., 836.

of the question); for, if the fatty glycerides themselves are sensibly attacked by the chlorine after the colouring matters have been destroyed, the resulting soap is apt to " work foxy "—*i.e.*, either to become brown in the pan during boiling or to darken in colour subsequently when cut up into bars. On the other hand, the unpleasant odour of rancid tallow and grease from tainted or putrid carcases, tannery refuse, and such-like materials is apt to be communicated in some degree to the resulting soap unless the grease is previously deodorised by chlorine, etc.

In many cases a great improvement in odour may be brought about by simply blowing steam through the melted grease for some time, the volatile malodorous matters present being thus, to a large extent, expelled.

With rank fish oils larger proportions of bleaching powder are necessary (as much as 1 per cent. and upwards), with an equivalent quantity of sulphuric acid. The bleaching powder is made into a milk with water and well intermixed with the oil, which is slightly heated by blowing in a little steam; the acid diluted with several times its volume of water is then run in with vigorous agitation. Finally, steam is blown through and the whole allowed to rest and subside.

Chlorine bleaches wax readily, but chloro-substitution products are apt to be formed, so that, if the bleached wax is used for making tapers or candles, hydrochloric acid vapours are evolved when these are burnt, causing considerable annoyance.[1]

Cotton-seed oil in the raw state contains a peculiar colouring matter capable of being dissolved out together with resinous matters by agitation with aqueous solutions of caustic alkalis (p. 347). Sometimes this purification is only partially carried out, the residual colouring matter being distroyed by boiling with a dilute solution of bleaching powder and treatment with dilute sulphuric acid. The oils thus more or less completely refined and decolorised by chemicals are, as a rule, only used for soap-making and similar technical purposes; whereas those completely refined by soda alone are used as edible oils, being largely employed for cooking purposes, and to a great extent mixed with olive and other high-priced " salad " oils. As a rule, each oil refiner has his own particular special methods of effecting the final clarification and finish of such superior products, which are looked upon as valuable trade secrets.

Dark-coloured soaps are sometimes bleached more or less completely by intermixing with the hot curd freed from lye, a solution of " chlorine of soda " (bleaching powder made into a cream and treated with enough carbonate or silicate of sodium to remove all lime from

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[1] The important chemical discovery that " electropositive " hydrogen could be replaced in organic compounds by highly " electronegative " chlorine without materially altering the character of the substance affected, was first made in consequence of investigations carried out by Gay Lussac in order to elucidate the cause of this occurrence in the reception-rooms of the Emperor Napoleon I., where wax candles were largely burnt.

solution). This may be effected in the pan itself, but is best done by crutching the liquid into the soap in the frame (*A. Watt*); the precipitated calcium carbonate or silicate need not be previously removed. If made from coarse rank " goods," the soap will be largely deodorised by the process.

Hydrogen-Peroxide Process.—The bleaching action of hydrogen peroxide on certain forms of organic colouring matters has long been known and utilised in certain cases where the cost was not prohibitive—*e.g.*, in the manufacture of various high-priced toilet fluids for converting the pigment in dark hair into one of golden hue, or even bleaching it completely white. Notwithstanding improvements whereby the cost of manufacture of hydrogen peroxide is greatly reduced, this substance is still too expensive for use on the large scale for low-priced oils, etc., although in many cases it is well fitted for the purpose.

Drying oils required for artists' varnishes are sometimes bleached by floating them in a thin layer on the surface of hydrogen peroxide dissolved in water, the whole being warmed and, if possible, exposed to sunlight to facilitate the operation. By being shaken up repeatedly in a closed vessel with about $\frac{1}{20}$ part of a 10 per cent. solution of hydrogen peroxide, most oils can be rapidly bleached, or at least greatly lightened in colour.

Wax Bleaching by Exposure to Air.—The effect of light and air on beeswax in removing the natural yellowish tinge is utilised in the following manner:—The wax is first melted and boiled up with water acidulated with a small quantity of sulphuric acid (about 1 part by weight of oil of vitriol per 1,000 of wax); impurities are thus washed out, and a clear bright melted wax obtained. This is then run from a sort of cullender pierced with holes on to a drum half immersed in a tank of cold water. As the streams of fluid wax come in contact with the cool wet surface they solidify into thin ribbons, which are scraped off the drum after they have passed down under the water so as to complete their solidification. Finally, the ribbons are spread out in thin layers on canvas sheeting, and placed in the open air so as to be exposed to the sun and air. After a time, the partially-bleached ribbons are remelted and again cast into ribbons, and exposed for a further period, the whole operation lasting several weeks according to the weather and the nature of the wax, some kinds yielding much more rapidly to atmospheric oxidation than others. Usually, only the outer portions of the ribbons become bleached, the action not penetrating far into the interior; so that to expose the whole equally to light and moisture, the mass requires to be turned over from time to time and sprinkled with water. Obviously, the thinner the ribbons are the better.

Japan Wax.—In the purification of Japan wax a very similar process is adopted. The crude wax, as obtained from the dried berries of the *Rhus succedanea*, is melted and strained, and allowed to drip into water kept agitated so that it solidifies in thin flakes. These are then exposed to sun and air in trays, being now and then sprinkled with water and turned over; the vegetable colouring matter present in the crude wax is thus readily blanched, an almost white product being obtained.

In the case of some varieties of beeswax this result cannot be so readily secured, the colour sometimes not yielding at all readily to atmospheric influences. Addition of a small quantity of fatty matter to beeswax often facilitates the bleaching action of the atmosphere under the influence of sunlight. According to some authorities, this does not improve the quality of the wax, whilst the presence of glycerides is usually regarded as proof of adulteration. On the other hand, *A.* and *P. Buisine* (*infra*) state that the addition of 3 to 5 per cent. of tallow, is universal amongst French air-bleachers in order to prevent the product becoming brittle, and is not regarded at all as an adulteration. A small percentage of oil of turpentine is sometimes used instead of fatty matter. The volatile hydrocarbon escapes to a large extent during the process by exposure to air; but a small quantity becomes resinised by oxidation and retained by the wax; probably this oxidation gives rise to hydrogen peroxide in minute quantity, which assists the bleaching action.

According to *A.* and *P. Buisine*,[1] the chemical bleaching of beeswax is always accompanied by an increase in the acid value, and a diminution in the iodine value, indicating the direct addition of oxygen to the unsaturated acids present. Thus the following figures were obtained in a long series of experiments :—

	Iodine Absorbed by 100 Parts of Wax.	Total Acid Value.
Pure yellow waxes, ...	10·87-11·23	91-95
Pure air-bleached waxes, ...	6-7	93-100
Air-bleached, with addition of 3 to 5 per cent. of tallow, ...	6-7	105-115
Air-bleached, with addition of 5 per cent. spirit of turpentine, ...	6·78	100·4
Bleached by hydrogen peroxide, ...	6·26	98·4
Decolorised by permanganate, ...	2·64-5·80	92·2-103·3
Decolorised by bichromate, ...	1·08-7·94	98·9-107·7

On the other hand, decolorisation by means of animal charcoal caused no marked alteration in either the acid value or the iodine absorption.

An indirect method of bleaching by means of air is sometimes practised, especially with linseed oil. The oil to be treated is agitated at intervals with ferrous sulphate solution. This has a tendency to become oxidised by absorption of oxygen from the air, whilst the resulting ferric compound parts with oxygen to the colouring matter,

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[1] *Bull. Soc. Chim.*, 1890, iv., 465.

oxidising the latter and blanching it, becoming itself again reduced to the ferrous state; and so on continuously.

Action of Artificial Light.—A process protected by *Stanley* and the *Cotton-seed Oil Syndicate* (Eng. Pats. 11,419 and 17,443, 1901) consists in circulating the oil in a thin film over a transparent surface, and subjecting it to the action of artificial light during its passage.

In the apparatus used for this purpose the oil is placed in a tank with a conical lower end which is closed. Three bleaching chambers, consisting of a series of vertical posts supporting glass sides and closed with an air-tight cover, are fixed above this tank; whilst above these chambers is a second tank, connected with a pump which draws the oil from the lower tank. The oil is sprayed against the glass sides of the chamber by means of fan-shaped distributors, and eventually falls into the lower tank through pipes that project a short way into the bottom of the chambers, and are controlled by valves. The light for bleaching the oil is furnished by electric arc lamps within the chambers, and it has been found by experience that three lamps of 1,500 candle power will bleach the oil flowing over an area of 400 square feet in five to eight hours. When required, the oil in the lower tank is heated by means of a steam coil, and appliances are also provided for cooling the bleaching surfaces.

Several other processes involving the use of ultra-violet light have also been devised (German Pats. 195,665 and 223,419).

DEODORISING AND REMOVAL OF RANCIDITY.

Numerous methods are in use for deodorising fresh fats, such as coconut oil, or for treating rancid fats so as to remove the objectionable constituents. Dry heat, superheated steam, oxidising agents of various kinds, hydrogen, animal charcoal, alkalis, and various salts are used as the active agents in different processes.

Thus, *Andreoli* (Eng. Pat. 14,570, 1898) uses ozone in conjunction with a hypochlorite solution to effect both deodorisation and decolorisation.

In another process, also protected by *Andreoli* (Eng. Pat. 14,569, 1898), the oil or fat is melted in water and continually agitated with a dilute solution of a sulphide, sulphite, or hypochlorite (preferably the hypochlorite of zinc, aluminium, ammonium, or especially magnesium). Finally the fat is washed with water.

Culmann (Eng. Pat. 26,191, 1897) effects deodorisation by subjecting the fat to the simultaneous action of steam at 108° to 110° C., and of a saturated solution of alum or aluminium sulphate. The oil is kept at a temperature of about 80° C. until the sediment deposits, after which the clear upper layer, which is now odourless, is withdrawn. Oil thus treated is said not to resume its odour on warming, even in the case of fish oils.

In *Filbert's* process (Eng. Pat. 5,197, 1895) the oil is heated in a hot-water jacketed cylinder, converted into spray by means of paddle wheels, and a current of air blown through the spray.

Catalytic hydrogenation of fats effects deodorisation as well as hardening (see Chap. xv.), and the same result may be obtained by the action of hydrogen under pressure in the absence of a catalytic agent.

Deodorisation of Coconut Oil.—*Schlink's* method for removing the volatile and odorous fatty acids, etc., from coconut oil, consists of treating it with alcohol and animal charcoal, so as to obtain a perfectly white mass of the consistency of butter and of a sweet, neutral flavour. This product has a considerable sale as a "vegetable lard" for cooking purposes, and is also doubtless extensively used in the adulteration of butter.

Ruffin has patented the following process of preparing an edible fat from coconut oil (Eng. Pat. 1,827, 1896):—The oil is allowed to stand for about forty-eight hours at its melting point (23° C.), and the crystalline portion, which amounts to about 45 per cent., separated by means of a filter-press. The dry cakes are then melted and treated with lime, and the emulsion evaporated *in vacuo* with continual agitation at a temperature not exceeding 20° to 25° C. Finally, the fat is separated from the calcium soap by pressure, again melted, treated with lime, and evaporated. The fat when separated from the excess of lime and calcium soaps melts at 31° C.

According to *Stanley* (Eng. Pat. 5,907, 1898) coconut oil is readily deodorised by being boiled with water containing a suitable proportion of potassium or sodium silicate, say, 1 part of silicate to 32 parts of fat.

Coconut oil of inferior quality may be greatly improved by being boiled with about $\frac{1}{30}$ of its weight of soda lye (sp. gr. 1·03) for half an hour, with frequent skimming. Some 4 or 5 lbs. of salt per ton of oil are then added, and the boiling continued for another half hour. Another equal quantity of salt is then added, and the whole boiled up; and, after standing till next day, the cleansed oil is run off from the brine and foots that have subsided.

Removal of Rancidity.—Sometimes it is required to treat oils that have become more or less rancid by keeping, owing to fermentative changes, atmospheric oxidation, or other causes, but from which most of the mucilage, etc., originally present has been already removed. In such cases thorough agitation with a weak solution of sodium hydroxide, or a somewhat stronger one of sodium carbonate, suffices to remove the free fatty acids of low molecular weight (butyric, caproic acids, etc.) that are present, as well as others, if already formed by hydrolysis; and to dissolve out most, if not all of the malodorous non-acid products of decomposition, so as to sweeten the oil. Diluted milk of lime and calcined magnesia are sometimes used in a similar fashion.

As a rule, oils that have once become rancid, even if pretty thoroughly sweetened by such refining, are more apt to turn rancid again on keeping than fresh ones.

In some cases agitation with water alone without alkalis suffices to wash out the objectionable decomposition products to a considerable extent. Thus rank butter is greatly sweetened by simply being thoroughly worked about and washed in water.

In a process protected by *Harris* and *Headington* (Eng. Pat. 19,085, 1898) the oil is treated with prepared chalk and then heated at 110° to 130° F. with animal charcoal in the proportion of 1 cwt. to the ton. After being separated from the charcoal, it is heated at a temperature not exceeding 110° F. with methylated alcohol containing 1 per cent. of gum myrrh and 0·5 per cent. of gum benzoin, and allowed to stand at 100° F. This treatment is said to impart a nutty flavour.

Harris and the Globe Trading Company (Eng. Pat. 9,252, 1898) have protected a process that is stated, not only to remove rancidity, but also to combine different grades of fat into a uniform quality. The oil or fat is first emulsified by being heated at 110° to 130° F. with liquids, such as a 10 per cent. solution of sodium chloride or a 1 per cent. solution of sulphuric acid in water or milk, etc. After standing for twelve hours at a temperature not less than 100° F., the fat is aërated by a current of air at a temperature of 120° to 140° F. in the presence of a suitable quantity of "washing liquid," such as a more dilute solution of sodium chloride or sulphuric acid, this treatment being repeated as often as required.

Nagel has based the following process of purification on his method of separating the different constituents of rancid fats (p. 185) :—The fat or oil, after purification with sulphuric acid, is heated and mixed with a concentrated solution of soluble glass, the amount of which is proportional to the quantity of free fatty acid present.

The heavy precipitate is filtered off, and the residual oil boiled for six hours with dilute sulphuric acid. When cold the oil is separated from the acid and again washed with a solution of soluble glass.

It is next heated with a fourth of its weight of a mixture of sodium carbonate and milk of lime (1 : 1), and filtered from the small amount of saponified oil that sinks to the bottom. When cold, the filtered oil is treated with a fourth of its weight of a concentrated solution of sodium bisulphite, the aqueous layer separated, and the oil heated in a still with steam, the temperature of which is gradually raised. Finally, it is cooled in a current of carbon dioxide.

CHAPTER XII.

RECOVERY OF GREASE FROM "SUDS," ETC.

In certain textile industries, more especially the woollen manufacture, and to a somewhat less extent the silk and cotton industries, the materials are treated at particular stages of the process with soap liquors for the purpose of washing out impurities of various kinds; whilst in various dyeing operations soaping is also resorted to for the purpose of clearing off superfluous dyestuff, cleansing the undyed portions, and so on. Formerly, the "soap suds" thus produced were thrown away, being conducted into the nearest available stream, etc.; but the great amount of river pollution thus brought about has in many cases rendered it imperative that at least some amount of purification of such liquors should be effected before they are thus run away; whilst the value of the fatty matters saved by adopting proper processes for such purification, often renders it profitable to employ such methods, even when so doing is not otherwise compulsory.

The methods adopted necessarily vary to some extent with the nature of the materials to be dealt with. In cases where coloured waste liquors from dyeworks, etc., constitute the great bulk of the substance to be treated, the cheapest and most satisfactory methods appear to be modifications of the precipitation processes employed in similarly dealing with sewage. Thus by adding a small proportion of milk of lime to the liquors, and simultaneously running in a solution of crude aluminium sulphate,[1] the alumina and ferric oxide precipitated by the lime unite with the colouring matters forming "lakes," which ultimately subside by gravitation in suitable settling tanks, carrying down mechanically with them various other impurities (albuminoid matters, fatty acids, etc.), so as finally to yield a clear almost colourless effluent containing in solution only non-precipitable matters, such as alkaline salts, etc.

The "sludge" thus resulting is usually of but little value, even for manure. When, however, soap suds constitute a sufficiently large proportion of the waste liquors, it is preferable to collect and treat these *separately* so as to recover the grease, the slightly acid watery liquors left after this operation being either run away directly, or,

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[1] Alumino-ferric cake containing somewhat large amounts of iron, chiefly obtained from the mother liquors of purer aluminium sulphate made by treating bauxite, clay, etc., with sulphuric acid. The use of ferric hydroxide for the removal of oil from water has recently been patented by *Breda* and *Holz* (Eng. Pat. 4,670, 1900). In *Dehne's* process (Eng. Pat. 21,131, 1894) a cream of hydrated alumina is added to the greasy water, and the mixture passed through the filter-press.

preferably, mixed with the coloured waste liquors, and the whole treated together as above described. A little more lime is required in this case to neutralise the free acid contained in the grease recovery liquors, and this must be added before the alumina can be effectively precipitated from the sulphate. The precise details of the method of working necessarily vary in each instance; but it is within the author's (Alder Wright) knowledge that processes substantially of the character described could be so worked as to answer the purpose in most satisfactory fashion, especially when carefully carried out under pressure of an impending injunction.

Two methods of treating soap suds are thus applicable. In one the soap is made to react upon a lime compound, such as thin milk of lime or solution of calcium chloride, so as to form insoluble lime soaps by double decomposition. These are collected by subsidence and filtration (the more or less purified liquor being run away), and subsequently decomposed with sulphuric or hydrochloric acid so as to liberate the fatty acids, thus obtaining a more or less impure grease. After hot pressing or filtration the fatty acids are obtained separately from the solid matters admixed with them, and may be utilised in the production of rough soap, cart grease, etc., or submitted to distillation with superheated steam, according to their nature and degree of impurity.

This lime process is more especially applicable to comparatively dilute suds, etc., where the object is rather to get rid in some way or other of a dirty waste liquor which, from the circumstances of the case, *must* be somewhat purified before discharging, than to work a recovery process profitable in itself.

When, however, the soap liquors are more concentrated, it is preferable to use the other method, consisting of simple acidification of the suds with sulphuric[1] or hydrochloric acid; the fatty acids thus liberated would naturally float up as a sort of greasy scum, were it not for the presence of other heavier suspended matters which, in most cases, and more especially with wool scouring soap suds, render the total precipitate (" magma " or " coagulate ") somewhat heavier than the watery fluid, causing it to sink. This process is more especially employed in the recovery of " Wakefield fat " or " Yorkshire grease," which essentially consists not only of free fatty acids derived from soap, but also of wool-grease contained in the raw wool, and other oleaginous matters used in the spinning and weaving processes.

In the English woollen industry the method of cleaning wool usually adopted essentially consists in scouring with soft soap, or other soaps of special character; during the further processes through which the wool is put before it is finally converted into woven cloth, soap and oil are tolerably freely used in the spinning, fulling, and milling of the fibre, yarn, and cloth.

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[1] Chamber acid suffices, or acid from the Glover tower, rectified oil of vitriol being too costly, except in cases where the less cost of carriage of the smaller bulk outweighs the increased price due to the côst of further concentration.

The soap suds and similar waste liquors produced in these various operations are collected in large tanks or reservoirs, holding several thousand gallons, and acidulated with a mineral acid—*e.g.*, B.O.V. (brown oil of vitriol); after agitation and subsequent standing for some hours, a fatty " magma " or coagulate deposits at the bottom of the tank; the supernatant watery fluid (which should be slightly *acid*, otherwise the whole of the soap has not been decomposed) is then run off, and the tank filled up with fresh suds and acidulated as before, excepting that somewhat less acid is now requisite, owing to the smaller quantity of suds treated, the tank having been partly filled with magma and watery fluid (with a tank 6 feet deep, the magma, etc., usually fills up 15 or 18 inches).

The process is again repeated, the magma (known locally in Yorkshire as " sake ") being ultimately thrown on filter beds, where most of the remaining watery liquor separates, and then subjected to pressure in bagging. At first the pressure is very gently applied, so as to squeeze out water only, but subsequently it is increased and heat applied (hot press), so as to filter the fused mass through the bagging, furnishing a dark sticky grease, and a residual " sudcake " available as manure. The grease is what is properly called " Yorkshire grease ; " but similar recovered products (" Fuller's grease ") obtained by treating the soap suds produced in other industries where scouring with soap is largely employed, are sometimes included in the term (cotton industry, silk manufacture, dyeing, etc.).

Genuine Yorkshire grease from wool scouring essentially consists of the free fatty acids derived from the soap used, the wool-grease contained in the wool, and such unsaponified oil and mineral hydrocarbons, etc., as may have been used in the spinning and weaving operations for the purpose of oiling or sizing the yarn, etc.; whilst analogous greases from other sources are more or less different as regards the nature of the substances present other than free fatty acids.

According to *Lewkowitsch*[1] Yorkshire grease rarely, if ever, contains unsaponified glycerides, any glyceridic oils used in the spinning process becoming saponified during the after processes of washing, etc.; so that the essential organic constituents are—(1) free fatty acids, partly derived from the wool-grease, but chiefly from the soaps used in washing; (2) cholesterol and isocholesterol esters, and similar derivatives of other high alcohols—*e.g.*, cetylic and cerylic alcohols; (3) free alcohols (cholesterol, etc.) either naturally contained in wool-grease, or produced during scouring by the partial saponification of their compound esters; together with hydrocarbons contained in the oils used for greasing during spinning, etc.

Analysis of Yorkshire Grease.—The free acids are usually determined by titration in the usual way (p. 166), their average molecular weight being *assumed* to be some constant value—*e.g.*, 282 = oleic acid. Inasmuch, however, as they usually contain a notable amount of acids

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[1] *J. Soc. Chem. Ind.*, 1892, xi., 134.

of much higher molecular weight, derived from the wool-grease, this mode of calculation is apt to give too low a result.

In order to obtain a more exact valuation, the alcoholic soap solution thus formed may be diluted with water, and shaken with ether or light petroleum spirit, so as to dissolve out all other constituents (or better, evaporated to dryness and exhausted with ether or, preferably, light petroleum spirit (p. 170), as the ethereal and watery fluids are apt to form frothy emulsions, not readily separating into two liquids). The weight of the free fatty acids insoluble in water is then determined by acidification, etc., as in Hehner's process; by titrating these with alkali, and subtracting the amount neutralised from that neutralised during the first titration, the alkali equivalent to the soluble acids may be deducted; so that these latter may be calculated, assuming an average molecular weight—*e.g.*, 102 = valeric acid, $C_5H_{10}O_2$.

The sum of the cholesterol esters, etc., and unsaponifiable matters is obtained by weighing the ether or petroleum spirit extract; when only an approximately exact result is required, this may be determined by difference, the fatty acids found by titration (together with water, mineral matters, etc.) being subtracted from 100 (*vide infra*). The cholesterol esters are only saponified with great difficulty. The best method is to treat them under pressure with excess of double-normal alcoholic potassium hydroxide (in a tightly-closed vessel heated to 100° C.); in this way a measure of the amount of compound esters present is obtained,[1] so that by again *assuming* a mean molecular weight (*e.g.*, that of cholesteryl stearate, $C_{26}H_{43} . O . C_{18}H_{35}O = 638$), their amount may be calculated.

A preferable method, however, is to separate the soaps thus formed as before by means of ether, etc., dissolving out the alcohols formed by saponification (or pre-existing in the grease) and hydrocarbons, etc.; the fatty acids contained in the soaps are separated and weighed, and the alcohols, etc., obtained by evaporating off the solvent. The acetyl test applied to this residue allows an estimation to be made of the alcoholiform constituents, again assuming a mean molecular weight—*e.g.*, that of cholesterol, $C_{26}H_{44}O = 372$, whence the amount of hydrocarbons present is known by difference.

The figures thus obtained will then come out as follows:—

FIRST TREATMENT.

A	B
Free fatty acids insoluble in water (weighed). ,, ,, ,, soluble in water (calculated from difference of titration).	Compound esters, alcohols, and hydrocarbons (weighed).

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[1] If substances analogous to stearolactone (p. 45) are present, or organic anhydrides (possibly present in *distilled* grease), alkali is also neutralised by them during this operation.

SECOND TREATMENT OF B.

C	D
Fatty acids contained in compound esters (weighed).	Alcohols (pre-existing and formed by saponification) and hydrocarbons (weighed). The former calculated as $C_{26}H_{44}O$ from the acetyl test; the latter by subtracting the quantity thus found from D.

Since water is taken up during the saponification of the compound esters, the sum of the organic constituents thus reckoned should exceed 100, as in the parallel case of soap, when the total alkali and fatty acids present are determined.

For certain purposes, more especially the preparation of "lanolin" or similar cholesterol products of more or less purity, the proportion of alcohols present regulates the value of the material more than does the amount of fatty acids. The presence of hydrocarbons (whether intentionally added as ingredients in the oiling process during spinning, etc., or due to adulteration of the oils thus used with petroleum products or rosin oils, or formed during distillation of grease, the "oleine" thereby obtained, *vide infra*, being used for wool-oiling) considerably depreciates the value of the material for these purposes; in many cases the presence of such substances in the extract D obtained as above can be indicated, and the amounts roughly judged, by treating this residue with alcohol or glacial acetic acid, in which solvents the hydrocarbons are only sparingly soluble.

For many purposes a less troublesome method of analysis suffices. Thus, *Lewkowitsch* (*loc. cit. supra*) recommends the following process for the examination of Yorkshire grease:—About 5 grammes are titrated with alcohol and semi-normal alkali; another portion is similarly titrated by boiling with excess of alkali (*i.e.*, the "acid value" and the "saponification value" are determined); the difference between these titrations gives a measure of the compound esters, glycerides, and other saponifiable matters present.

By means of ether (or, preferably, light petroleum spirit), the "unsaponifiable matters" (alcohols, hydrocarbons, etc.) are dissolved out and weighed, whilst the "insoluble fatty acids" and "volatile" acids are determined by the Hehner and Reichert-Meissl processes (pp. 234, 241). Thus, a sample of Yorkshire grease yielded the following results:—

Unsaponifiable matters (weighed), ...	36·47	per cent.
Free fatty acids; insoluble (weighed—Hehner value), .	20·22	,,
Free volatile acids (calculated as $C_5H_{10}O_2$), . . .	1·28	,,
Combined fatty acids (calculated from difference of titrations, assuming the mean molecular weight = 327·5), ...	48·47	,,
	106·44	,,

The excess of 6·44 per cent. thus found is partly due to the water taken up during hydrolysis of the compound esters; probably also the assumed mean molecular weight of the combined fatty acids (327·5) is somewhat too high. On the other hand, the value 282 (oleic acid) would be too low.

In the determination of the unsaponifiable matters present, *Mansbridge*[1] recommends in place of ether the use of light petroleum spirit (prepared by redistilling commercial benzoline and collecting the part distilling at about 110° F. = 43° C.). The grease is saponified with excess of alcoholic potassium hydroxide (under pressure if required), and the product decomposed with mineral acid, whereby a mixture of free fatty acids and unsaponifiable matters is obtained. Of this a portion sufficient to yield about 0·5 gramme of unsaponifiable matter is dissolved in 50 c.c. of methylated spirit saturated with benzoline distillate, and 50 c.c. of that distillate added; the whole is heated just to the boiling point, directly neutralised with semi-normal potassium hydroxide, and then transferred to a separating funnel, where the hot petroleum spirit solution of unsaponifiable matter and the alcoholic soap solution rapidly separate from one another.

The alcoholic soap solution is run off, 50 c.c. of water at 100° F. (37·8° C.) added, and the whole agitated to wash out any soap dissolved by the petroleum spirit. After separating by standing, the watery fluid is run off, and replaced by 40 c.c. of warm 70 per cent. alcohol: this, when agitated with the petroleum spirit, removes the last traces of dissolved soap. The alcoholic soap solution first run off is agitated a second time with petroleum spirit, and the petroleum spirit solution purified as before: for some kinds of grease more than two such extractions are necessary, but, as a rule, two suffice.

The percentage of unsaponifiable substances (including cholesterol, etc., produced by decomposition of cholesterol esters) thus found is not far removed from, though usually somewhat less than, that calculated by assuming that the fatty acids present (free and combined as cholesterol esters, etc.) have the mean molecular weight 282 (oleic acid), and subtracting their weight (together with water, suspended matters, etc.) from 100. Thus *Mansbridge* gives the comparative results in the table on the next page.

According to *Hess*,[2] the difference between the amounts of unsaponifiable matters obtained in these two ways gives a rough valuation of the cholesteroid bodies present, the proportion of these latter being approximately found by multiplying the difference by 10.

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[1] *Chemical News*, 27th May, 1892.

[2] *J. Soc. Chem. Ind.*, 1892, xi., 144.

	Unsaponifiable Matters.	
	By Extraction as above.	By Titration, &c.
Pure wool-fat, ...	29·05 29·25	39·36
,, ,, another sample, ...	41·70 41·70	46·79
West of England recovered grease, . . .	21·55 21·05	23·16 23·16
,, ,, ,, ,, another sample,	22·81	23·63
Distilled wool-fat, ...	52·25 51·90	48·64 48·64
Oleine from distilled wool-fat, ...	44·35 44·25	44·31
,, ,, ., another sample, .	50·25 50·35	47·13
Black grease recovered from shoddy scourings,	22·61 22·72	25·55

The following analyses of Yorkshire grease (method of analysis not stated) are given by *Hurst*[1] as fairly typical :—

	1	2	3	4
Specific gravity at 15·5° C., .	0·9391	0·9417	...	0·9570
,, ,, 98° C., .	0·8900	0·8952	...	0·8720
Water, ...	0·98	1·53	1·21	0·94
Fatty acid, ...	18·61	24·25	24·15	26·43
Neutral oil, ...	68·62	58·25	30·02	16·86
Unsaponifiable oil, . . .	11·68	15·83	44·44	55·77
Ash, ...	0·11	0·14	0·18	trace
	100·00	100·00	100·00	100·00

Thus, the higher the density, the greater the percentage of unsaponifiable oil. Such greases generally melt at about 44° C. ; they can be saponified with alkalis, but only imperfectly. The flash point is usually near 220° C.

Distilled Grease.—Yorkshire grease from wool, and analogous recovered greases from other sources, are rarely sufficiently free from odour and otherwise of general good character to enable them to be directly used for anything but the coarsest purposes—*e.g.*, as cart grease, and similar rough lubricating materials, such as that required for the hot axles of tin-plate rolling machines.

When subjected to distillation in cast-iron[2] stills of about 1,000 gallons capacity, holding about 4 tons of grease, a variety of products

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[1] Cast iron is much less rapidly corroded by the fatty acids than wrought iron —*vide* Hurst, *loc. cit. supra.*

[2] *Ibid.*, 1889, viii., 90.

is obtained, to some extent varying with the quality and nature of the grease. The stills are first heated for 10 to 16 hours with free fire to drive off water, and then for 20 to 24 hours more with superheated steam, during which time a pale yellow product comes over, known as "first distilled grease," sometimes preceded by a lighter "spirit oil," sometimes not.

After the "first distilled grease," "green oil" comes over, sometimes used for coarse lubricating greases, but more often put back into the still and worked over along with the next batch. Finally, the distillate comes over as a thick oil, and the operation is then regarded as finished; the fires are drawn, the superheated steam turned off, and the pitch run out of the still.

Yorkshire grease thus treated gave the following percentage results:—

Pitch,	14·1 parts.
Green oil,	15·5 "
First distilled grease,	45·5 "
Spirit oil,	4·1 "
Water and loss,	20·8 "
	100·0

The pitch thus obtained forms a useful lubricant for the necks of hot rollers.

The "first distilled grease" is sometimes allowed to "seed" or crystallise in the usual way (Chap. XVII.), and then pressed in a hydraulic press, so as to obtain a liquid "oleine" and a solid "stearine" in about the relative proportions of 2 to 1. The oleine that exudes spontaneously from the crystallised cake before pressing is sometimes collected apart and designated "No. 1 oil," or the grease is distilled a second time, so as to obtain about 96 per cent. of "second distilled grease," and 4 per cent. of "soft pitch."

The "spirit oil," as it first runs from the stills, is pale yellow in colour, but darkens on keeping, probably by oxidation, like the somewhat analogous oils obtained on the redistillation of bone tar and other products of destructive distillation. It contains a small quantity of free fatty acids, equivalent to 4 or 5 per cent. of oleic acid; on redistillation, it begins to boil at about 150° C., about two-thirds distilling below 240° C., and seven-eighths below 320° C. It finds a limited use in making black varnish.

From what constituent of the original grease it is derived is not known with certainty. Possibly it is formed from cholesterol, etc., but as hydrocarbons are always formed in small quantity in the redistillation of "red oils" (crude oleic acid) and similar substances containing little or no constituents analogous to cholesterol, it is more probable that it comes from the decomposition of the oleic acid present.

"Distilled grease" is of pale yellow colour, and of granular texture. *Hurst* obtained the following results in the analysis of two samples:—

	First Distilled Grease.	Second Distilled Grease.
Water, ...	0·98	1·04
Free acid, . . .	63·12	66·56
Unsaponifiable matter, . .	12·88	13·24
Neutral oil, . . .	23·02	19·16
	100·00	100·00

Lewkowitsch found a considerably larger percentage of hydrocarbons in a sample of distilled grease examined by him, viz. :—

Free fatty acids (molecular weight = 286), . . .	54·91 per cent.
Combined fatty acids (molecular weight = 327·5), . .	7·02 ,,
Unsaponifiable matters, ...	38·80 ,,
	100·73 ,,

The combined fatty acids would represent about 11·28 per cent. of compound esters (" neutral fat "), leaving 34·54 per cent. of hydrocarbons.

The " stearine " obtained from distilled grease by pressure is a hard pale yellow greasy solid; that from " first distilled grease " is darker than that from " second distilled grease," but has usually a slightly higher melting point. Apparently the fatty acids present have a higher molecular weight than stearic acid, inasmuch as the free acid found on analysis, when calculated as stearic acid and added to the other constituents, gives a total considerably under 100 (*Hurst*).[1] Thus—

	Stearine.	
	From First Distilled Grease.	From Second Distilled Grease.
Specific gravity at 15·5°, . . .	0·9044	0·9193
,, ,, 98°, . . .	...	0·836
Water, ...	1·48	0·6
Free acid calculated as stearic acid,	76·3	88·6
Unsaponifiable oil, ...	0·4	0·49
Neutral oil, ...	7·7	2·11
	85·88	91·80
Melting point, ...	57° (134° F.)	48° (118° F.)
Solidifying point, ...	53·5° (128° F.)	45° (113° F.)

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[1] The presence of stearolactone might possibly explain the apparent deficiency in free acids.

The oleine simultaneously obtained is pale when fresh, but gradually darkens, probably owing to the presence of iron derived from the press or the tanks in which it is stored. It is generally known in the district of production as "wool oil," because it is chiefly used for oiling woollen yarns, etc. Lubricating greases and soaps are sometimes prepared from it; but for the latter purpose it is not at all well suited on account of the large proportion of unsaponifiable matter.

It varies much in composition, even when from the same maker, on account of the varying composition of the Yorkshire grease originally employed. Thus, the neutral oil varies between 9 and 28 per cent., and the unsaponifiable oil between 10 and 38, whilst the free acid (calculated as oleic acid) constitutes 53 to 65 per cent. The flashing point usually lies between 322° F. and 342° F. (*Hurst*).

Engine Waste Grease and Fuller's Grease.—The grease recovered from greasy engine waste (p. 321) is closely akin to that obtained from soap suds; but owing to the large use of hydrocarbons as ingredients in lubricating oils at the present day, it is usually much less valuable, the yield of solid "stearine" being but small, and the "oleine" containing large quantities of unsaponifiable hydrocarbons. When the spindles, etc., are lubricated with tolerably pure vegetable oils or with sperm oil, etc., a much better form of grease results; but this is comparatively rare.

Grease recovered from silk soap suds and soap baths from cotton dyeing works, etc., usually consists of free fatty acids with but little unsaponifiable matter, and is often clean enough to be used directly for soap-making.

Its commercial valuation for such purposes is generally effected by determining the percentage of water present, and of substances insoluble in alcohol (unsaponifiable matter), subtracting the sum from 100, and reckoning the difference as available fatty acids.

When too dirty for use in even the coarsest soap, such grease is either directly utilised for lubricating materials of the roughest kind, or is distilled by means of superheated steam, and the distillate pressed for stearine and oleine.

§ 5. Classification and Uses of Fixed Oils, Fats, Waxes, &c.; Hydrogenated Oils; Systematic Description; Adulterations.

CHAPTER XIII.

CLASSIFICATION.

In accordance with their ordinary physical texture, sources (whether animal or vegetable), and essential chemical nature, the fixed oils, fats, butters, and waxes, etc., may be conveniently divided into twelve classes, falling into two principal divisions, according as the main components are of glyceridic or non-glyceridic nature.

Division I.—Essentially Glyceridic.

A. *Fluid at Ordinary Temperatures :—*

1. *Non-drying Oils—*
   - *Vegetable—*
     - (1) Olive (almond) class.
     - (2) Rape (colza) class.
     - (3) Ricinoleic (castor) class.
   - *Animal—*
     - (4) Lard oil class.
2. *Intermediate : Drying Qualities possessed to a limited extent :—*
   - *Vegetable—*
     - (5) Cotton (sesamé) class.
   - *Animal—*
     - (6) Train, fish, and liver class.
3. *Drying Oils : well-marked Drying Qualities :—*
   - *Vegetable—*
     - (7) Linseed class.

B. *Solid or Semi-solid at Ordinary Temperatures :—*

- *Vegetable—*
  - (8) Palm butter, and Japan wax class.
- *Animal—*
  - (9) Tallow, lard, and cow's butter class.

Division II.—Essentially Non-Glyceridic.

A. *Fluid at Ordinary Temperatures :—*

Animal—

(10) Sperm oil class.

B. *Solid or Semi-solid at Ordinary Temperatures :—*

Vegetable—

(11) Carnauba wax class.

Animal—

(12) Beeswax and spermaceti class.

CLASS I.—OLIVE (ALMOND) CLASS.

A large number of oils are known completely fluid at ordinary temperatures and not congealing until greatly chilled, consisting chiefly of olein with smaller quantities of more solid glycerides (myricin, palmitin, stearin, arachidin, etc.), and in some cases small admixtures of glycerides of other kinds. As a rule, however, glycerides of the "drying oil" division are only present in very small quantities, so that oils of this class are practically *non-drying*.

The presence of the other constituents raises the relative density somewhat above that of pure olein (near 0·905 at 15° C.), usually to between 0·913 and 0·924; and at the same time tends to diminish the iodine value below 86·2 per cent., the calculated value for pure olein, excepting in those cases where a material quantity of less saturated glycerides is present, when the superior iodine absorbing power of these ingredients slightly raises the value instead of lowering it. The calculated saponification equivalent of pure olein is 294·7; that of an oil of this kind generally differs but little therefrom, being a little higher or a little lower, according as the other constituents have mean equivalent weights above or below this value. The proportion of glycerides other than those of oleic and the solid fatty acids is not large enough to interfere with the production of a tolerably hard solid elaidin with nitrous acid, nor to cause that heat evolution on mixture with sulphuric acid to be large.

The chief oils of commercial or local importance belonging to this class that have been investigated to any extent are as follows :—

Name of Oil.	Source.
Almond (sweet), . . .	*Amygdalus communis* (*Prunus amygdalus*), var. *dulcis*.
,, (bitter), . . .	,, ,, ,, var. *amara*.
Arachis (ground-nut), . .	*Arachis hypogœa*.
Ben, ...	*Moringa pterygosperma ; M. aptera* (*Guilandia moringa*).
Hazel-nut, ...	*Corylus avellana*.
Olive, ...	*Olea Europœa sylvestris ; O. E. sativa*.
Plum-, peach-, cherry-, and apricot-kernel oils, .	*Prunus domestica ; P. persica ; P. armeniaca ; P. cerasus ; P. brigantiaca ; P. serotina*.
Tea-seed, ...	*Camellia theifera ; C. oleifera ; C. drupifera*.

Besides these, however, a large number of oils are in use to varying extents in different countries for edible purposes, burning, anointing, etc., many of which agree in their general physical characters with the above, more especially in being practically non-drying in character and only solidifying at low temperatures, and hence presumably consisting essentially of olein; the chemical examination of many of these, however, has not yet been undertaken; and as yet they are but little exported, and consequently have not found their way into general trade in any large quantities (*vide infra*).

Vegetable Expression Oleines.—Semi-solid vegetable tallows and butters, when subjected to cold pressure, yield a solid mass of higher melting point, together with a comparatively fluid oil or oleine. In certain cases, more especially for the production of the higher fatty acids for candle-making, this treatment is resorted to in order partially to separate the more fluid glycerides from the others. Coconut oil and palm-kernel butter when thus treated yield fluid oleines, solidifying a few degrees above 0°; these consist partly of oleic glyceride, partly of the glycerides of the acetic series of lower molecular weight contained in the original butters; and, in consequence of the presence of these latter in considerable quantity, possess a somewhat different composition from ordinary oils of the olive class—*e.g.*, the iodine absorption is much lower (often below 30 to 40) owing to the relatively small amount of oleic glyceride present; and similarly, the heat development on mixture with sulphuric acid is below that observed with olive oil (coconut oleine = 26° to 27° C.; olive oil = 41° to 43° C.—*Allen*). On account of the absence or minute proportion of linolenic and similar glycerides, these products are almost completely non-drying.

CLASS II.—RAPE (COLZA) CLASS.

The characteristic property of this class of oils is that of possessing a much higher saponification equivalent than the oils of Classes I. and III. in virtue of the presence of considerable quantities of a higher homologue of oleic acid—viz., *erucic acid*, $C_{22}H_{42}O_2$, crystallisable and melting at 34° C. In the case of colza oil another acid, rapic acid, $C_{18}H_{34}O_2$, isomeric with oleic acid, has been stated to be also present in considerable quantity (p. 34). More precise information, however, is decidedly wanted as regards the constituents not only of the less known members of the group, but also of those most commonly occurring.

The specific gravity is relatively low, usually below 0·918; the saponification equivalent usually lies between 315 and 325; whilst the iodine value is between 95 and 105, indicating the presence of a certain amount of glycerides of linolic character,[1] a result also borne out by the possession of some degree of drying character by the oils themselves, not, however, of a strongly marked kind, and by the formation of insoluble bromides.

Oils of this class do not give a particularly solid elaidin reaction

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[1] The calculated value for erucin is 72·4, that for olein 86·2.

with nitrous acid, butter-like masses being usually formed which often separate on standing into two portions, one solid and the other liquid.

The principal oils of this class are those mentioned in the following table, but in all probability many of the less known oils are of similar composition, judging from their general physical characteristics :—

Name of Oil.	Source.
Colza (rape) oil, . . .	Different cultivated varieties of *Brassica campestris.*
Hedge-mustard (hedge-radish oil), ...	*Raphanus raphanistrum* (*Raphanistrum arvense*).
Mustard (black and white); Chinese cabbage oil), . .	*Sinapis nigra* ; *S. alba* ; and other species of *Sinapis.*
Radish, ...	*Raphanus sativus.*

CLASS III.—CASTOR OIL CLASS.

In this class of oils the prevailing glyceride is that of a hydroxy acid, such as ricinoleic acid, which gives to oils of this description peculiar chemical characteristics. Comparatively few oils besides castor oil have been sufficiently closely examined to render it certain that they belong to this class; but it is highly probable that several of the less known oils used locally for edible purposes, or as lamp oils, in different parts of the world, really consist of a greater or less extent of hydroxy acid glycerides. Thus, " Louc Muc " seed oil, which is obtained from a plant in Annam, resembles castor oil in being miscible with alcohol in all proportions. Its iodine value is about the same as that of olive oil.

A tolerably high specific gravity, from 0·950 to 0·970, is possessed by oils of this class, and a saponification equivalent of 305 to 315 (calculated value for ricinolein = 310·67). The elaidins are soft and buttery. The following oils appear to contain more or less considerable proportions of hydroxy acid glycerides :—

Name of Oil.	Source.
Castor, ...	*Ricinus communis* (var. *minor and major*).
Curcas (purqueira oil), . .	*Jatropha curcas* (*Curcas purgans*).
Grape-seed, ...	*Vitis vinifera.*

CLASS IV.—ANIMAL NON-DRYING OILS—LARD OIL CLASS.

When comparatively solid animal fats are subjected to a regulated pressure (p. 312), a mechanical separation of the solid and liquid constituents is effected if the temperature be suitably adjusted. The fluid subtances thus expressed are, strictly speaking, the only products to which the term " oleine " is applicable (besides the analogous fluid constituents of vegetable oils); but in commercial practice the fluid free fatty acids separated by similar means from the products of saponification of such fats, are also designated " oleins," as also are the analogous fluid acids obtained from steam-distilled fatty acids from greases of various kinds (p. 348). Further, oils treated with sulphuric acid (Turkey red oils) are often termed " oleine " in the cotton-dyeing industry. Accordingly, the glyceridic expression products are more usually spoken of as " oils " (*e.g.*, tallow oil) than as oleines; although, even then, confusion is not always avoided, since the terms " tallow oil " and " red oil " are sometimes also applied to the expressed crude oleic acid of the candle-maker.

Products of this class closely resemble vegetable oils of Class I., especially when free from any animal or rancid odour betraying their origin. According to the way in which the expression is effected (more especially as regards temperature), they contain varying quantities of the solid constituents (" stearines," chiefly palmitin and actual stearin —*i.e.*, stearic glyceride) in solution, but otherwise consist essentially of olein (oleic glyceride). They usually have a specific gravity of about 0·915 or 0·916 at 15° C., and solidify within a few degrees of 0° C. (above or below). With nitrous acid they form firm solid eladins; with sulphuric acid (Maumené's test) the heat evolution is small, as compared with most other oils. The chief oils of the class are :—

Name of Oil.	Source.
Lard, ...	Hogs' lard subjected to expression.
Neat's foot, horse foot, sheep's trotter,	The "feet" (hoofs and hocks) of oxen, horses, and sheep.
Tallow, ...	Ox and mutton tallow subjected to expression.

CLASS V.—SESAMÉ OR COTTON-SEED CLASS—VEGETABLE SEMI-DRYING OILS.

The distinctions between this class of oils and those of Classes I. and VI. are not always very clearly marked, the differences being rather of degree than of kind, chiefly consisting in the presence of distinctly larger proportions of glycerides of the drying class than are present in non-drying oils of Class I., although these ingredients are not contained is sufficient quantity to give true drying qualities, such as are possessed by oils of Class VI.—*i.e.*, the power of absorbing oxygen from the air, and becoming a solid varnish-like mass. Accordingly, the effect of the elaidin test (*q.v.*) is to form a soft solid mass, far inferior in hardness and consistency to that furnished by typical non-drying oils, such as olive or arachis oil, but considerably more solid in character than the soft nearly fluid products formed by the true drying oils, such as linseed oil.

In general, the specific gravity at 15° C. is a little higher than that of oils of Class I., in most cases lying between 0·923 and 0·935; and the iodine absorption is similarly raised considerably above 86·2, the theoretical value for pure olein. In most cases, solid glycerides (palmitin, stearin, etc.) are present to a greater or less extent, together with small quantities of glycerides of hydroxy acids. The following are the best known oils of the class:—

Name of Oil.	Source.
Beech-nut, ...	*Fagus sylvatica.*
Cameline (German oil of sesamé or gold of pleasure oil), .	*Camelina sativa.*
Cotton-seed, ...	*Gossypium herbaceum*; *G. hirsutum*; *G. barbadense*; *G. arboreum*: *G. religiosum.*
Cress, ...	*Lepidium sativum.*
Madia, ...	*Madia sativa.*
Maize, ...	*Zea mais.*
Sesamé (gingelly oil, til oil, benné oil), ...	*Sesamum orientale.*
Soya bean, ...	*Soja hispida.*

Less Known Vegetable Oils.—In addition to the leading vegetable oils above mentioned belonging to Classes I., II., III., and V., a large number of other oils are locally known and used to a considerable extent in various parts of the world. In many instances little is known as to the chemical constitution of these substances; judging from their general physical characters they are, as a rule, either non-drying oils of the olive class, or semi-drying oils of the cotton-seed type; some, however, in all probability are more or less akin to rape or to castor oil.

The seeds of various species of pine (*Pinus sylvestris*, *P. abies*, *P. picea*) furnish by expression or solvents imperfectly drying oils used to some extent for burning and other purposes; these vary in specific gravity from 0·925 to 0·931 at 15° C., and mostly thicken at about − 15° C., solidifying at about − 27° C.

Croton oil, from *Croton tiglium*, is possessed of weak drying characters, but has a composition differing in many respects from most of the oils of the non-drying and semi-drying classes. The specific gravity of the fresh oil is 0·942 at 15° C., older oil that has absorbed oxygen from the air being more dense (about 0·955). Solidification occurs at about − 16° C. The oil is strongly purgative when taken in small doses internally, and vesicatory when applied to the skin; it does not form any solid elaidin with nitrous acid. It mainly consists of glycerides, and on saponification furnishes stearic, palmitic, myristic, lauric, caproic, valeric, butyric, acetic, and formic acids of the acetic family, together with tiglic (methyl crotonic), and crotonic acids of the oleic series. Oleic acid has been stated to be present by some investigators, and to be absent by others, a non-volatile " crotonoleic acid " yielding a barium salt soluble in alcohol having also been found. The vesicatory agent is believed to be " crotonol," a semi-solid body indicated by the formula $C_9H_{14}O_2$; this is not identical with the purgative principle, the nature of which is uncertain.

The seeds of *Ceratotheca sesamoides*, a plant growing on the Gold Coast, yield an oil with a nutty flavour, and having analytical values similar to those of sesamé oil (iodine value 110·6). Although so closely allied to the oil from sesamé seed, this oil does not give the Baudouin reaction.[1]

An excellent fatty oil is largely used in Morocco, derived from the Argan tree (*Argania sideroxylon, Elæodendron argan*, or *Sideroxylon spinosum*): the fruit is fleshy and is eaten greedily by sheep and goats, cows and camels, but the kernels or stones are hard and bony, and are consequently rejected by the animals. These stones are collected and cracked, and the inner white kernels carefully roasted, ground, and kneaded with a little warm water, whereby the oil is gradually expelled, more water being added from time to time, and the mass kneaded until no more oil exudes. After settling, the oil is a clear, light-brown fluid, often of somewhat rancid flavour and odour; it is largely used by the Moors as an edible oil, somewhat cheaper than olive oil. Somewhat similar oils are obtained from the kernels of the fruit of *Staphylea pinnata* (bladder-nuts) in Eastern Europe; the berries of the dogwood (*Cornus sanguinea*) in Italy, Cashmere, and Siberia; the seeds of the spindel tree (*Euonymus europæus*) of Central Europe; horse-chestnuts (*Æsculus hippocastanum*); and the seeds of *Sarcostigma Kleinii* (known as Adul or Odal oil in Southern India), of several *Hibiscus* species, and of *Pentaclethra macrophylla* (Owala oil of the Gaboon, Opochala oil of Fernando Po).

The Brazil nut or Castanha (*Bertholletia excelsa*) of South America yields a clear yellow bland oil closely resembling that of almonds, soon becoming rancid. The edible seeds of the *Telfairia pedata* of South-east Africa furnish a similar oil, said to be equal to the finest olive oil; and an oil of the same character is extracted from Paradise nuts, the seeds of *Quatele zabucajo*, a tree indigenous to Brazil and Guiana. Pumpkin-seed oil (*Cucurbita pepo*) is a clear sweet-tasting oil, yellowish or nearly colourless when obtained by cold pressure, possessed of only faintly marked drying qualities; its relative density is 0·923 at 15° C.; at − 15° C. it solidifies to a greyish-yellow mass.

Similar oils are obtainable from the seeds of other cucurbitaceous plants—*e.g.*, the water-melon (*Cucumis citrullus*), sweet melon (*C. melo*), gherkin (*C. sativus*), colocynth (*C. colocynthis*), etc. The oil of the Boma nut (*Pycnocoma macrophylla*) is sweet and bland, and is much used for cooking by the natives of Central Africa; that of the Cashew

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[1] Bolton, *Analyst*, 1919, xliv., 233.

or Acajou nut (*Anacardium occidentale*) is similarly employed in the East and West Indies and the West Coast of Africa; in the Brazils it has been in use for centuries as an edible oil; it is a light yellow sweet-tasting oil much like that of almonds, of relative density 0·916.

Mango seeds (*Mangifera indica*) and pistachio-nuts (*Pistachia vera*) yield similar oils, as also do the fruit kernels of *Buchanania latifolia*, a forest tree common in Coromandel, Malabar, and Mysore; the oil from the last is limpid and of a pale straw colour and is sometimes known as *Chironji oil*. Various species of *Œnocarpus* bear oleaginous nuts furnishing sweet cooking and eating oils, known in Para as "coumu oil," resembling olive oil but becoming solid much more readily on chilling. Hickory nuts (*Carya olivæformis*), M'poga nuts (common in the Gaboon), bread-nuts (*Omphalea diandra* and *O. triandra* —St. Domingo and Jamaica), and many other less known nuts and seeds are also sources of similar products.

A large number of new oil seeds have come into the English market from the West Coast of Africa, but the supplies have mostly been intermittent; some few are particularly well adapted for use were a constant supply forthcoming, more especially the seeds of the *Telfairia occidentalis* (a cucurbitaceous plant; the *Myristica angolensis* (a scentless nutmeg); the *Hyptis spicigera* (a herbaceous labiate plant); the *Polygala rarifolia* ("Maluku" seeds); the *Lophira alata* ("Meni" or "Laintlaintain" seeds, from one of the *Dipterocarpeæ;* Senegambia and Sierra Leone); and the *Pentaclethra macrophylla* (a leguminous tree, the "Owala" of the Gaboon, and the "Opachala" of the Eboe country. "M'poga," "Mabo," and "Niko" nuts also furnish oils of a character that might render them very useful.[1]

Cây-doc oil, which is largely used by the Tonkinese for illuminating purposes, is extracted from the seeds of the *Garcinia tonkinensis*, a tree of the *Clusiaceæ* family. It contains a large proportion of olein and about 5 per cent. of a resinous oil. The soap resembles that of palm oil. The tree only begins to yield seed after twenty years, and but little of the oil or seed is exported to Europe.

Similar remarks apply to the oil-bearing produce of many other countries; in many instances the oils thence obtainable are of characters so good for a variety of purposes as to leave little doubt that a considerable trade in such materials will hereafter be developed whenever the conditions are realised necessary for the economical growth of the trees and plants, and the harvesting of their seeds, nuts, or other fruits, etc., or for their treatment on the spot for the extraction of oil; together with the necessary opening up of the districts for transport purposes, so as to enable regular supplies to be obtained. In all probability the uncertainty as to what quantity of material could be obtained, and its price, has largely militated against the importation into Europe of numerous raw materials of the kind, manufacturers not caring to expend time, skill, and capital in working up saleable products until assured on these points.

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[1] See Jackson, *J. Soc. Arts*, 1891, xl., 122.

CLASS VI.—DRYING OILS—LINSEED OIL CLASS.

The drying oils proper principally differ from the semi-drying oils in containing much larger proportions of the glycerides of the more "unsaturated" acids (linolic, linolenic, and isolinolenic acids), these substances greatly predominating, and only comparatively small amounts of olein and of the glycerides of the solid fatty acids being present, so that these latter rarely separate in any quantity as solid "stearines" on chilling and standing.

Owing to the more or less considerable amount present of these unsaturated constituents, both drying and semi-drying oils possess higher iodine absorbing powers than the oils of the first four classes, and develop more heat on mixture with sulphuric acid (Maumené's test). When drying oils are spread out in a thin layer they rapidly absorb oxygen from the air, increasing in weight and "drying up" to a solid varnish, which in time becomes perfectly hard and not in the least sticky or "tacky;" semi-drying oils, similarly treated, increase in weight to a much less extent, and more slowly, and never dry up thoroughly to a hard varnish free from stickiness. With nitrous acid, drying oils give no solid elaidins; semi-drying oils usually give buttery masses from which fluid matter separates (see p. 199).

The specific gravity of drying oils is usually distinctly higher than that of oils of Class I., generally lying between 0·923 and 0·935, and increasing as oxidation goes on, until finally the dried films or "skins" are heavier than water.

As Hazura pointed out, the drying qualities are the more pronounced the larger the proportion of linolenic and isolinolenic acids present, linolic acid contributing less markedly to the drying properties; so that an oil consisting mainly of the glycerides of oleic and linolic acids, even when the latter predominates, does not exhibit drying powers equal to that of another containing a considerable proportion of linolenic and isolinolenic glycerides. They regard non-drying, semi-drying, and drying vegetable oils as distinguishable by the following characters so far as liquid constituents are concerned :—

Non-Drying Oils contain none, or at most only small percentages, of the glycerides of either linolic, linolenic, or isolinolenic acids.

Semi-Drying Oils contain more or less considerable amounts of linolic glyceride, but little or no glycerides of linolenic or isolinolenic acid; the drying action being also retarded by the presence of more or less olein and other non-drying glycerides.

True Drying Oils contain considerable amounts of linolenic and isolinolenic glycerides, together with linolin, and but small amounts of olein and non-drying glycerides.

Obviously the exact lines of demarcation between non-drying and semi-drying oils, on the one hand, and between semi-drying and truly drying oils, on the other, are but faintly traced; so that it often happens that a given oil is classed by one writer amongst the oils of one class, and by another amongst those of the adjacent class.

Benedikt and *Hazura* were unable to obtain any sativic acid on oxidising the fatty acids of animal oils with alkaline permanganate, and therefore concluded that linolic acid was not a constituent of these oils. *Fahrion*, however, detected linolic acid in lard, and in fact it appears to be present in small quantities in all animal fats (*cf.* p. 161).

It has been shown by *Hehner* and *Mitchell* that drying oils, and in particular linseed oil (*q.v.*), yield insoluble bromine derivatives. *Halphen* has also devised a modification of their test for the detection of drying oils and marine animal oils in other oils.

The best known drying oils are the following :—

Name of Oil.	Source.
Hemp-seed, ...	*Cannabis sativa.*
Lallemantia, ...	*La lemantia iberica.*
Linseed, ...	*Linum usitatissimum* (*L. perenne*).
Niger-seed, ...	*Guizotia oleifera.*
Perilla oil, ...	*Perilla ocimoides.*
Poppy-seed, ...	*Papaver somniferum* ; *P. rheas* ; *Glaucium luteum* ; *Argemone mexicana.*
Sunflower, ...	*Helianthus annuus* ; *H. perennis.*
Tobacco-seed, . . .	*Nicotiana tabacum.*
Tung oil, ...	*Aleurites cordata.*
Walnut (nut), . . .	*Juglans regia.*
Weldseed, ...	*Reseda luteola.*

Many other oils of pretty strongly marked drying qualities are known and employed locally, without being articles in which any considerable amount of export trade is done ; few of these have been submitted to any detailed examination. Hickory-nut oil (*Carya olivæformis*) is sometimes solid under the name of "American walnut oil," but appears to be very inferior in drying qualities. Cedar-nut oil is another drying oil of the same character.

The first of a species of *Parinarium* growing in Sierra Leone, and known as Po-Yoak nuts, yield an oil with good drying properties (iodine value 156·9).

The seeds of *Calophyllum inophyllum*, a forest tree widely distributed in the eastern tropics, furnish an oil known by various names (dilo, domba, pinnay, poon seed, or tamanu oil) ; when mixed with pigments, this forms a paint that dries in twelve hours, without any previous boiling ; owing to the large yield of oil, and the plentifulness of the tree in India, Ceylon, the Malay Archipelago and Java, and the South Pacific Islands, etc., this oil appears likely to be an important article in future.

Sanga-sanga nuts (*Ricinodendron Africanua*), growing in Lower and French Congo, yield a pale yellow oil characterised by its abnormally high refractive index (1·5028 at 19·5). It dries more rapidly than linseed oil.

The oil from an allied species of plant, *Ricinodendron rautenii*, has an iodine value of 128·5, and has excellent drying properties. Locally the seeds are known as "manketti nuts."

Stillingia oil, which is present in the kernels of *Stillingia sebifera* to the extent of about 19 per cent., has an iodine value of 160, and resembles linseed oil in its general character.

The kernels of the *Aleurites cordata* (*Elæococca vernicia*) furnish an oil ("Japanese wood oil," "tung oil") largely used as a varnish in China and Japan on account of its extremely rapid drying qualities. According to *Cloez*, this oil contains about 25 per cent. of olein, and 75 of a homologue of linolin, furnishing on saponification elæomargaric acid, $C_{17}H_{30}O_2$.[1]

"Benefing" oil, obtained from a plant growing wild in the Niger district and in Madagascar, is used locally as a substitute for linseed oil.

CLASS VII.—TRAIN, LIVER, AND FISH OILS.

The term "train oil," strictly speaking, applies to any oil extracted from the blubber of cetaceans and allied marine mammalia (such as the seal, porpoise, dolphin, walrus, etc.), and, therefore, in the widest sense includes the sperm oil class, No. X.; but in the present connection it is intended to apply only to those blubber oils that are essentially of glyceridic character, and not to those that mainly consist of compound esters of monohydric alcohols. It is not quite the equivalent of the German term "thran," which also includes fish oils (sardine oil, menhaden oil, etc.) as well as liver oils (cod-liver oil, sunfish-liver oil, etc.).

Oils of this class have been much less thoroughly examined as to their chemical constitution than their importance as trade products warrants. In some cases they consist mainly of the glycerides of homologues of oleic acid; but other glycerides are generally present as well, preventing the formation of solid elaidins; soft products from which liquid matter separates on standing are generally formed, much as in the case of the oils of Classes II. and VI.; from which circumstance, together with the high iodine number generally indicated, and the possession of some degree of drying qualities, it appears probable that drying-oil glycerides are also present.

Liver oils (cod and shark's livers, etc.) generally contain considerable amounts of cholesterol and allied biliary products; like fish oils proper (*e.g.*, menhaden oil), they evolve much heat on admixture with sulphuric acid, resembling the vegetable drying oils in this respect; whilst train oils (whale oil, seal oil, etc.) give a somewhat lower degree of heat evolution, probably on account of the presence of notable amounts of the glycerides of solid fatty acids (stearin, etc.). Many of them

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[1] *Comptes Rendus*, lxxxiii., 943 (*cf.* Chap. xv.).

contain a considerable amount of an unsaturated hydrocarbon (*squalene*, see p. 20).

Marine animal oils resemble linseed oil in yielding an insoluble derivative on treatment with bromine, and the fatty acids yield an analogous compound, which in some cases is the octobromide of clupanodonic acid (*cf. Cod-liver Oil*, Chap. XVI.).

When oils of this class are separated from the nitrogenous tissues immediately, so that no decomposition takes place, they are comparatively inodorous and tasteless, and contain no appreciable quantity of free fatty acids; but if the livers, blubber, fish, etc., are kept for any length of time before the oil is extracted, a more or less strongly marked animal fishy smell is developed, becoming excessively rank in extreme cases; as in the case of rancid vegetable oils, more or less hydrolysis of glycerides, with production of free fatty acids, appears to accompany the development of the strong-smelling by-products thus formed.

The distinction between oils of this class (mainly glyceridic in character) and those of Class X. (mainly glyceridic) is in actual practice not very sharply marked; for sperm oils usually contain small quantities of glycerides, although the chief constituents are non-glyceridic compound esters; whilst on the other hand, some of the blubber oils contain notable amounts of solid non-glyceridic compound esters (spermaceti), deposited on cooling and standing. In fact, it is as difficult or impossible to draw a hard and fast line of demarcation between the glyceridic and non-glyceridic animal oils, as it is between the drying and non-drying vegetable oils; and for the same reason—viz., that whilst the two extremes are fairly sharply contrasted in general composition—yet various intermediates exist, partaking of the character of both classes. To some extent, this may possibly arise from the circumstance, that when a ship is engaged in oil-fishery, it is not always practicable to keep apart the blubbers obtained from different species, so that the oil ultimately extracted is often a mixture of the products obtained from different kinds of animals, each of which, if examined separately, would exhibit special characteristics analogous to those distinguishing different seed oils.

In general, it appears that whalebone-yielding whales[1] (*Balænoidea*) furnish oils containing little, if any, monohydric compound esters like spermaceti; whilst toothed whales (*Delphinoidea*) yield oil in which these substances are usually present, in some cases as chief constituents; these latter form the oils of Class X.

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[1] *Huxley* classes the existing cetacea (exclusive of extinct genera) as *Balænoidea* and *Delphinoidea*, the latter group including *Platinistidæ*, *Delphinidæ* (dolphins, porpoises, grampus, and narwhal) and *Physeteridæ;* these last being further subdivided into *Physeterinæ* (cachalots or sperm whales) and *Rhyncoceti* (bottlenose whales).

The chief oils of this class are the following :—

Name of Oil.	Sources.
Train Oils—	
Dolphin and Porpoise oils,	*Delphinus phocæna* (*Phocæna communis*), or common porpoise. *P. orca*, or grampus. *Delphinus delphis*, or common dolphin. *Delphinus globiceps*. *D. tursio*. *Monodon monoceros*, or narwhal.
Seal oils, ...	*Phoca vitulina; P. grœnlandica; P. barbata; P. annelata; P. lagura; P. fœtida; P. caspica; P. proboscidea*. *Otaria jubata*. *O. australis*.
Walrus oil, . . . (morse oil, dugong oil, manatee oil).	*Trichechus rosmarus*, morse or walrus. *Halicore australis* and *H. indicus*, or dugong. *Manatus australis* and *M. americanus*, or manatee.
Whale oils and Black-fish oils, ...	*Balænus mysticetus* or *B. grœnlandicus*, the "right whale." *B. glacialis*, or polar whale. *B. böops*, or humpbacked whale. *B. antarctica*, or Cape whale. *B. australis*, or southern black whale. *Balænoptera gibbar*, or finner whale. *Globiocephalus intermedias*, or pilot whale. *G. macrorhyncus*, or killer. *Beluga catodon*, or white whale.
Liver Oils—	
Cod oils, ...	*Gadus morrhua* (*Asellus major*). *G. cellarius*. *G. molva* (*Molva vulgaris*). *G. æglefinus*. *G. carbonarius* (*Merlangus carbonarius*). *G. merlangus* (*Merlangus vulgaris*). *G. pollachius* (*Merlangus pollachius*). *Merlucius communis*.
Malabar oils, . . .	*Rhyncobatus pectinata*. *R. laevis*. *Galeocerda tigrina*. *Carcharias melanopterus*.
Ray and Shark oils, .	*Raja clavata*. *R. batis*. *Trigon pastinaca*. *Squalus carcharias*, or common shark. *S. maxima*, or basking shark. *S. glacialis*, or Greenland shark. *S. zygæna* (*Zygæna malleus*), or hammerfish. *S. acanthias*, or picked dogfish. *S. spinax niger*, or kulp.
Fish Oils—	
Herring oils, . . . (sardine, sprat, pilchard, anchovy, louar, &c.)	*Clupea pontica* (Astrakan herring). *C. sardinus*, or sardine ; *C. neohouri*, *C. lemuru*, and *C. palasah*, or Indian and Malayan louar. *C. sprattus*, or sprat. *C. pilchardus*, or pilchard. *Engraulis encrasicholus*, or anchovy.
Menhaden oil, . . .	*Alosa menhaden* (*Brevoordia menhaden*).
Oolachan oil, . . .	*Thaleichthys paciferus osmerus*.
Tunny oil, . . .	*Thynnus vulgaris*.

Schädler gives the following table of colour reactions of seal, whale, liver, and fish oils with strong nitric acid (sp. gr. 1·45) ; sulphuric acid (sp. gr. 1·6 to 1·7) ; and the two mixed in equal proportions.

Nitric Acid	Sulphuric Acid.	Mixed Acids.
SEAL OIL— Red brown, . .	Reddish yellow, becoming reddish brown, and ultimately brownish red, somewhat like blood.	Reddish, becoming brown.
WHALE OIL— Brownish, becoming full brown, and finally black brown.	Brown, becoming black brown.	Yellow, becoming reddish, and finally dirty brown.
LIVER OILS— Blood red, becoming brownish red to brown.	Violet to black violet.	Yellow red, becoming bright red, finally reddish brown with violet streak.
FISH OILS— Brown, . . .	At first greenish, then brown, and finally quite black.	Yellow, then greenish, afterwards brown.

CLASS VIII.—VEGETABLE BUTTERS, FATS AND WAXES, ETC.

When the proportion of glycerides of relatively high melting point to olein is large, the physical texture of a substance that would be an oil in the tropics becomes more like that of butter at 15° to 20° C. Concurrently with the change in comparative fluidity, the iodine absorption is largely reduced, as compared with oils of Classes I. and VI., on account of the diminished proportion of olein present.

In the case of certain vegetable glyceridic waxes (*e.g.*, Japan wax), the olein is reduced to insignificant proportions, with the result of increasing the relative solidity and considerably raising the melting point.

Some of the substances of this class contain a notable proportion of glycerides of acids of the acetic group of sufficiently low molecular weight to be readily volatile with steam at ordinary pressure (*e.g.*, coconut oil, laurel butter, and palm-kernel fat); others are practically free from such ingredients. When subjected to regulated pressure (p. 343), liquid oleines are squeezed out and solid stearines left, the former closely resembling oils of Classes I. and VI. when sufficiently freed from the latter.

The best known substances of this class are contained in the table on following page.

Similar solid or semi-solid vegetable fats are also furnished by the following trees and plants:—

Nephelium lappaceum (Linn.); indigenous to Sunda Island, Malacca, and some parts of China. The seeds furnish "Rambutan tallow," melting at about 65° C., the solid stearine of which consists chiefly of the glyceride of arachidic acid; a little olein is also present (*Oudemanns*).

Name of Butter, &c.	Sources.
Bassia fat; Illipé butter, Mahwa butter, Phulwara fat (Fulwa fat), Shea butter (Galam butter), etc.	*Bassia latifolia* (Roxb.). *B. longifolia* (Linn.). *B. butyracea*. *B. Parkii* (*Butyrosperma Parkii*—Kotschy).
Cacao butter,	*Theobroma cacao* (Linn.). *T. bicolor* (Humb.). *T. angustifolium* (Sessé). *T. leiocarpium* and *T. pentagonum* (Bern.). *T. microcarpium* (Mart.).
Chinese tallow,	*Stillingia sebifera* [*Croton sebiferum* (Linn.)].
Coconut oil (copra butter or copra fat).	*Cocos nucifera*; *C. butyracea*.
Cotton-seed stearine,	Cotton-seed oil by chilling and pressing.
Dika fat,	*Irvingia barteri* (Hook.). *Mangifera gabonensis* (Aubry le Comte).
Japan wax,	*Rhus succedanea* (Linn.). *R. acuminata* (De C.); *R. vernicifera* (De C.); *R. juglandifolia* (Don.) *R. sylvestris* (Siebold).
Malabar tallow (Piney tallow)	*Vateria indica* (Linn.). *V. malabarica* (Blum.). *Elæocarpus copaliferus* (Retz).
Myrtle wax,	*Myrica cerifera* and several other species of myrtle.
Myristica butters (Nutmeg butter, Virola tallow, Otoba wax, Ucuba or ocuba wax, etc.).	*Myristica officinalis* (Linn.); *M. moschata* (Thumb.); *M. sebifera* (*Virola sebifera*); *M. otoba* (Humb. and B.); *M. ocuba* (*M. ucuba*, *M. bicuhyba*); *M. malabarica*.
Palm butter (palm oil). Palm-nut butter (palm-kernel oil).	*Elais guineensis* (Jacq.); *E. melanococca* (Gaert.); *Alfonsia oleifera* (Humb.), and many other species of palm (see Chap. XIII.).

Carapa guyanensis (*C. guineensis*) and *C. indica* (or *C. moluccensis*); found in Brazil, Guiana, Guinea, Sierra Leone, India, Ceylon, etc. The seeds of these two species yield about 70 per cent. of "Carapa fat" (otherwise designated "Andiroba fat," "Coundi oil," "Crabwood oil," "Touloucoona oil," etc.), possessing a composition akin to that of palm oil—*i.e.*, consisting chiefly of the glycerides of palmitic and oleic acid. It usually possesses a sickly persistent odour almost impossible to remove. The coloured natives use it largely as an unguent and insectifuge for the head, its properties in this respect being apparently due to an admixed bitter principle termed *carapin*. It is also used in the manufacture of soap.

Mafureria oleifera (Bert.) or *Trichelia emetica* (Vahl.). This tree grows in Mozambique, and about the Zambesi and the White Nile; by crushing the seeds and boiling with water, a fat known as "Mafura tallow" is obtained, much resembling cacao butter, melting at 42° C., and chiefly consisting of palmitin and olein.

Calophyllum inophyllum (Linn.), indigenous to India and the Malay Archipelago, and *C. calaba*, found in the Antilles, yield respectively "Poona fat" ("poon-seed oil" or "Tacamahac fat") and "Calabar oil." The former is also known by various other names (*vide supra*).

Laurus nobilis, found largely in Southern Europe and Asia, yields "laurel butter" ("bayberry fat"), largely consisting of the glyceride of lauric acid, together with a little myristin and other homologues, and some olein. A similar product is obtained from *L. persea* (Linn.) or *Persea gratissima* (Gaert.) the Alligator pear tree of Brazil and the West Indies; known as "Alligator pear oil," "Persea fat," and "Avocado oil."

In addition to these, a large number of more or less hard vegetable fats and tallows are obtained from other sources, concerning the chemical constitution of which comparatively little is known. Thus, "Malayan tallow" and "Borneo tallow" are solid fats obtained from the nuts of various species of *Hopea* in Java, Sumatra, and Borneo. An analogous product, "Sierra Leone butter," is obtained in Sierra Leone from *Pentadesma butyracea*. "Goa butter" ("Kokum butter" or "Mangosteen oil") is a similar fat obtained in the East Indies from the seeds of *Garcinia indica* (*Mangosteena indica*). The allied species *G. pictoria* or gamboge tree furnishes "gamboge butter." The seeds of *Pongamia glabra*, another East Indian shrub, yield "Korinje (Karanja) butter," "Poondi oil" or "Ponga oil," which melts at a somewhat lower temperature than most of the vegetable fats and tallows.

"Macaja butter" is derived from the edible fruit of *Cocos aculeata Acromia sclerocarpa*, Mart.; *Bactris minor*, Gaert.), indigenous to Brazil, Guiana, and the West Indies. In Java a fat much resembling coconut oil, "tangkallak fat," is derived from the *Cylicodaphne sebifera*. Semi-solid fats are obtained from the *Canarium commune* of the Moluccas and Malabar ("Canary oil," "Java almond oil") and the butter-nut tree of the Brazils (*Rhizobolus butyrosa*); the allied species, *R. amygdalifera* (*Caryocar brasiliensis*) and *Caryocar tomentosum*, respectively furnish "Caryocar oil" and "Sawarri (or Souari) nut butter."

"Akee oil" is a yellow non-drying fat of the consistency of butter, extracted from the pulp of the seeds of the akee tree, which grows on the coast of Guinea. It has a bitter taste.

The soap tree of Bengal, Southern India, and the West Indies (*Sapindus emarginatus*, Roxb.; *S. trifoliatus*, Linn.; *S. laurifolia* Vahl.), furnishes a fruit rich in saponin, and also yields a semi-solid fat. "Maccassar oil" is a semi-solid fat obtained from the seeds of *Schleichera trijuga*;[1] and "Piquia oil" ("Pekea fat") is a similar product from *Pekea butyrosa* and *P. ternatea*, found in Guiana and the Antilles. *Melia azedarach* (Linn.), the "paternoster tree" of Syria, Northern India, and the Deccan, etc. (so-called from the employment of its stones in Italy and elsewhere for making rosaries), also known as *Melia indica* (Brand.) and *Azadirachta indica* (Juss.), furnishes a very similar semi-solid fat, known as "Zedrach oil," "Margosa oil," "Veppam fat," or "Nimb (or Neem) oil."

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[1] Also from the oleaginous fruit of *Stadmannia* (*Cupania*) *sideroxylon*, growing in Sunda and Timor Islands, and from the seeds of the safflower (*Carthamus tinctorius*); other varieties of so-called "Macassar" oil are simply more or less fluid oils in which odorous flowers, etc., have been digested so as to scent them.

"Niam fat" is derived from the *Lophira alata*, found in Eastern and Western Africa. "Chaulmoogra oil" is a soft fat or oil obtained from the seeds of *Taraktogenos Kurzii*, much used in India, China, and elsewhere for medicinal application to the skin. "Soudan butter" is a soft fat obtained by boiling with water the seeds of *Vitellaria paradoxa*, or Soudanese butter plant; a similar product is obtained in Cochin China and Japan from the seeds of *Sebifera glutinosa* (*Tetranthera laurifolia*, Jacq.). The seeds of *Œnocarpus bacaba* and *Œ. patawa*, of Central America, yield by similar treatment a soft fat known locally as "Comou butter."

"Para butter" or "Assai oil" is similarly obtained from the Assai palm (*Euterpe oleracea*), common in Brazil and the neighbourhood of Para. "Chequito" is a fatty substance obtained by the Kaffirs of South-East Africa from the "butter tree," *Combretum butyraceum*. The seeds of *Cocculus indicus* contain a solid fat, extracted and used by the natives in India, but apparently not yet known commercially; similar products are obtained from the fruit kernels of *Lucuma bonplandi* in Mexico, and the Ochoco (*Dryobalanops*) of Guinea.

Piassava oil, derived from a species of *Raphia*, growing in Sierra Leone, is a dark red fat resembling palm oil. (Iodine value 79·5.)

"Mkani fat," which is extracted from the seed of the S. African tallow tree, *Stearodendron Stuhlmanii*, is remarkable as the source of the mixed glyceride, oleo-distearin (*cf*. Chap. I.). Its iodine value is about 40.

"Maripa fat," obtained from *Palma maripa*, resembles coconut oil, and is used as butter in the West Indies. Its iodine value is 17·55.

A similar fat is expressed from the kernels of the seeds of *Acrocomia sclerocarpa*, which is indigenous to the West Indies. It closely resembles coconut and palm-kernel oils, and is known as gru-gru oil (*J. Soc. Chem. Ind.*, 1914, xxxiii., 9).

In addition to the above, a large number of other sources of vegetable fats exist in different parts of the world, the knowledge of which is as yet chiefly confined to the natives; there can, however, be little doubt that in due time, as civilisation advances and opportunities for export and manufacture become more frequent, many of these little-known products will be found to be of considerable value as sources of oleaginous material.

CLASS IX.—ANIMAL FATS—TALLOW, LARD, AND BUTTER CLASS.

Almost every known animal is capable of yielding more or less considerable amounts of fatty matter by appropriate treatment; but, in practice, comparatively few are actually employed as sources of fat, apart from their consumption as food. The solid fat of oxen and sheep (known as *tallow* or *suet* when derived from the adipose tissues of the body), the grease extracted from their hoofs (*neat's foot oil*, *sheep's trotter oil*), and that obtained by boiling the bones (*bone grease*) are closely akin in general composition, except that the latter are softer in character, chiefly because they contain a larger proportion of olein and a smaller amount of solid glycerides.

The fatty matters (butters) contained in the milk of cows and ewes, on the other hand, have a composition materially different from that of the fats present in the adipose tissues of the body; and the same remark applies to the milk fats of all other mammalia, so far as they have been examined.

In general, the milk fats of various animals do not differ very greatly in character; thus, the butters derived from the cow, ass, ewe, goat, elephant, hippopotamus, sow, mare, and woman, appear to be as closely akin as are the more or less solid tallows, greases, and suets obtainable from the body tissues of these various animals; but whilst the latter fats are all essentially mixtures of the liquid glyceride of oleic acid, and the solid glycerides of stearic and palmitic acids (the liquid constituents being present in larger quantity in the softer fats, like lard), the former fats contain a considerable amount of the glycerides of acids, also of the stearic series, but of much lower molecular weight than palmitic acid. Similarly, the milk fat of the whale is not widely different from that of the cow, although the oil of whales' blubber differs much from suet in composition.

The fats obtained from the carcases of birds (goose grease, turkey fat, pheasant grease, etc.) appear to be substantially similar to the softer body fats of mammalia in general composition, essentially consisting of olein, with enough stearin and palmitin to render them semi-solid at the ordinary temperature; the oleaginous matter contained in eggs (*e.g.*, hen's eggs) is softer still, and consists of olein and palmitin together with other substances foreign to the oil proper (*vide* Chap. XVI.).

The fat of certain wild animals and birds (hare, blackcock, etc.) has been found by *Amthor* and *Zink* to possess remarkable drying properties, rapidly yielding a dry film when exposed in a thin layer upon glass. This is probably due to the presence of a considerable proportion of linolenic acid, which has also been found in traces in other animal fats.

Various reptiles (turtles, crocodiles, etc.,) are utilised in different parts of the world as sources of oleaginous matters, apparently, for the most part, closely akin to the fats of the mammalian vertebrates; on the other hand, the oily matters derived from fish are differently constituted (*supra*).

The list on p. 388 includes the more important solid or semi-solid animal fats, apart from those derived from fishes and cetacea.

In addition to these, the fat of the alpaca is used to a considerable extent in some parts of South America; that of the dog in continental Europe, that of the hippopotamus in Africa, and that of the turtle in the islands of the South Pacific, Brazil, and along the South American coast. The last is sufficiently fluid in a tropical or subtropical climate to be used as a burning oil.

Name of Fat.	Sources.
Bone fat, ...	Bones of oxen and horses, etc., extracted by boiling or by solvents.
Butter (cow's milk fat), .	Domestic cow.
Butter substitutes (margarine, oleomargarine),	The softer portions of the fat of oxen and sheep, etc., separated by special processes.
Crocodile fat (alligator fat), .	Indian crocodile and common alligator (*Alligator lucius*).
Egg oil, ...	Yolks of hens' eggs (*Gallus domesticus*).
Goose grease, . . .	Common goose.
Horse grease (mare's grease),	Horse carcases (*Equus caballus*).
Lard, ...	Common hog.
Tallow, ...	Ox, sheep, goat, etc.
Tannery grease, kitchen grease, wool-grease,	Animal greases from various kinds of trade refuse.

Bear's grease was at one time highly esteemed as a pomade, but is now mostly superseded by other forms of clarified fat. Many other animal fats are also used locally in different countries to a greater or less extent, but as yet are not articles of regular trade. When the solid or semi-solid fats of this class are subjected to expression, the liquid animal oleines of Class IV. are obtained—*e.g.*, lard oil, tallow oil, etc.

CLASS X.—ANIMAL OILS—SPERM OIL CLASS.

The blubber oils included in Class VII. (whale, seal, porpoise, etc.) differ from those belonging to this class essentially in that they consist chiefly of fatty glycerides; whereas the oils now under consideration, whilst not invariably free from glyceridic constituents, have, as regards their leading constituents, an entirely different composition, these substances being compound esters formed from monohydric alcohols and fatty acids analogous to ethyl acetate and similar substances.

In general, two kinds of such compound esters appear to be present simultaneously—one liquid at ordinary temperatures, corresponding with the olein of ordinary vegetable oils, and consisting of esters of acids of the oleic group; the other solid, corresponding with stearin or palmitin, and consisting of esters of acids of the acetic group.

Just as a vegetable oil on chilling deposits solid matter of the stearin character, readily separable by filtration or straining, so does a blubber oil of the sperm class similarly deposit solid crystallisable matter, generally the substance known as *spermaceti* (mainly consisting of cetyl palmitate); the liquid portions separated from this deposit appear to be mixtures not only of compound esters of different homologous acids, but also of different homologous alcohols, some of which belong to the ethylic series, whilst others are apparently homologues of acrylic alcohol, capable of combining with iodine, like the unsaturated acids. In consequence, when saponified, these liquid oils yield large percentages of products insoluble in water, but soluble in ether, etc., consisting of mixtures of the alcohols formed during saponification; a circumstance sharply distinguishing them from the glyceridic oils of Class VII., which yield only comparatively small quantities of unsaponifiable matters insoluble in water, chiefly consisting of cholesterol and similar substances.

On account of the presence of compound esters of the oleic group, oils of the sperm class become more or less solidified by nitrous acid in virtue of the elaidin reaction; with Maumené's test they develop but little more heat than olive oil, being thus sharply distinguished from most fish oils of Class VII., which give a much greater heat evolution. Their peculiar compound ester composition largely raises the saponification equivalent.

The physical characters of this class of oils also are peculiar in virtue of their unusual constitution. Thus their efflux viscosity (*q.v.*) is much less influenced by variation of temperature than is the case with most other oils, whence their value as lubricants for special purposes. Their specific gravity is low, usually considerably below 0·900 and near 0·880.

The principal oils of this class are as follows:—

Name of Oil.	Sources.
Sperm, . . .	*Physeter macrocephalus*, L. (Cachalot whale).
Doegling (Arctic sperm or true bottlenose), .	*Hyperöodon rostratus* (*Balæna rostrata*), or true bottlenose whale, *H. bidens*.

Various other toothed cetaceans also furnish oils containing spermaceti in sufficient quantity to separate out in the solid state on chilling and standing, more especially the oil from the bottlenose dolphin, *Delphinus globiceps*, which appears to be essentially intermediate in character between the almost wholly glyceridic and largely valerin-containing oil from the common porpoise, and the mainly compound-ester sperm oil of the cachalot in which only small amounts of valerin are present.

CLASS XI.—VEGETABLE NON-GLYCERIDIC WAXES.

Several species of plants are known, the berries, leaves, stalks, etc., of which are naturally covered with a waxy exudation closely akin in its origin to certain of the more solid vegetable fats, but differing in being essentially non-glyceridic in character. Of these substances the principal are as follows:—

Name of Wax.	Source.
Carnauba, ...	*Corypha cerifera* (Linn.); *Copernicia cerifera* (Mart.).
Cow-tree, ...	*Galactodendron americanum* (Linn.); (*G. utile*, Kunth; *Brosimum galactodendron*, Don).

In addition very similar products are obtained from several other sources—*e.g.*, *Petha wax*, from the bloom on the Indian white gourd (*Benincasa cerifera*); *Fig wax* (Getah wax), prepared in Java and Sumatra from *Ficus umbellata* and *F. cerifera* (Blume); *Palm wax* (Ceroxylin), largely used in Brazil, from the common wax palm *Ceroxylon andicola* (Humb), and the Klopstock palm *Klopstockia cerifera* (Karsten); *Cordillera wax* from the Cordillera wax-tree (*Elæagia utilis*); and *Rhimba wax* obtained from the "Rhimba" tree (Madagascar).

These products, however, do not seem to have been submitted as yet to full chemical investigation, so that it is not certain whether they are true vegetable waxes of non-glyceridic character, or simply vegetable fats of waxy texture analogous to the so-called Japan wax. Comparatively little of these various kinds of vegetable waxes is as yet exported to Europe, most being used for candle-making, etc., in the countries where they are indigenous.

CLASS XII.—BEESWAX AND SPERMACETI CLASS.

The non-glyceridic wax-like compound esters of animal origin used to any extent industrially are but few in number, the principal being as follows:—

Name of Wax.	Source.
Beeswax (ordinary beeswax, Andaquia wax, Antilles wax, African beeswax, Abyssinian beeswax, &c.),	*Apis mellifera*, or common bee. Numerous allied species exist, many of which are also wax producers—*e.g.*, *Apis fasciata* (*Melipona fasciata*), or South American bee; *Apis unicolor*, or Madagascan bee; *Apis dorsata*, of the Eastern Archipelago. The common wasp and other allied genera are also wax producers to a limited extent.
Chinese wax (Peh-la or Pela),	*Coccus sinensis* (*Coccus pe-la*, *C. chinensis*).
Indian wax (Arjun wax), .	*Ceroplastes ceriferus.*
Niin fat, ...	*Coccus adipofera.*
Spermaceti, ...	*Physeter macrocephalus.*
Wool-grease, ...	Natural grease (inspissated perspiration) of the common sheep.

CHAPTER XIV.

PRINCIPAL USES OF OILS AND FATS, ETC.

The classification described in the previous chapter is mainly based on the physical and chemical characters of the natural fixed oils and allied substances. From the point of view of their leading practical uses they may be conveniently considered under one or other of the following six heads :—

1. Substances used for edible purposes, including cooking and preservation of food (*e.g.*, sardines).
2. Fluid oils employed for burning in lamps or otherwise.
3. Substances furnishing solid materials for candle-making.
4. Substances used in the manufacture of soap.
5. Drying oils obtained for paint manufacture and in the preparation of varnishes, linoleum, and such-like products.
6. Substances used for miscellaneous purposes ; more especially as lubricants or ingredients in lubricating mixtures ; for currying leather, dressing cloth and textile fabrics, and similar purposes ; as oil baths for tempering metals ; as solvents for odorous matters in the process of *enfluerage* in perfumery manufacture ; for the preparation of unguents, pomades, cosmetics, etc. ; in the manufacture of sealing wax and analogous compositions ; and for numerous minor uses in the arts generally.

Of these six groups, Nos. 3 and 4 are separately considered in § 6 and § 7 (candle- and soap-making, including glycerol extraction). With respect to the other uses, some few points are of special interest from the technological point of view, in connection with which the question of purity and freedom from adulteration with inferior materials is frequently of prime importance.

EDIBLE AND CULINARY USES OF OILS, FATS, ETC.

Fatty matters of various kinds are ingredients of most kinds of foodstuffs in common use to a greater or less extent. Thus apart from suet and the adipose tissues interlaminated with the "lean" of most kinds of animal meat, most vegetable seeds, nuts, and other edible produce contain more or less considerable quantities of oleaginous matter ; sometimes to an extent sufficiently large to admit of oil being extracted by pressure (*e.g.*, olives, walnuts, hazelnuts, etc.), sometimes only in smaller quantity, so that a solvent (ether, etc.) is required before the presence of oil can be demonstrated. When thus treated, however, even such substances as wheaten flour and cereal produce generally, rice, and dried vegetables can be shown to contain small quantities of oleaginous ingredients.

Apart from the consumption of oily matter for food in forms such as these, large quantities of separately extracted fatty substances are habitually used by both civilised and uncivilised races—*e.g.*, as "salad" oils employed for "dressing" raw vegetables and otherwise as food materials; more or less purified and rendered animal fats, especially dripping and lard; and the fatty matter of cow's milk (butter). In cold climates seal and whale oil are eagerly taken by the natives as heat-generating foods, whilst a lump of tallow is a delicacy; elsewhere fish preserved in oil (*e.g.*, sardines), or cooked in hot oil, pastry containing butter, suet puddings, and numberless other viands into the composition of which more or less oleaginous matter enters, are everyday articles of diet.

With the exception of actively medicinal oils (such as *croton* and *castor oils*), the great bulk of natural glycerides is suitable as food material for cattle, especially when used without separation from the other vegetable matters naturally accompanying them. *Linseed cake* (crushed linseed subjected to pressure so as to express most of the oil), and similar substances from other kinds of seeds, etc., are well known cattle foods, the value of which largely depends on the amount of residual oily matter left in the mass.

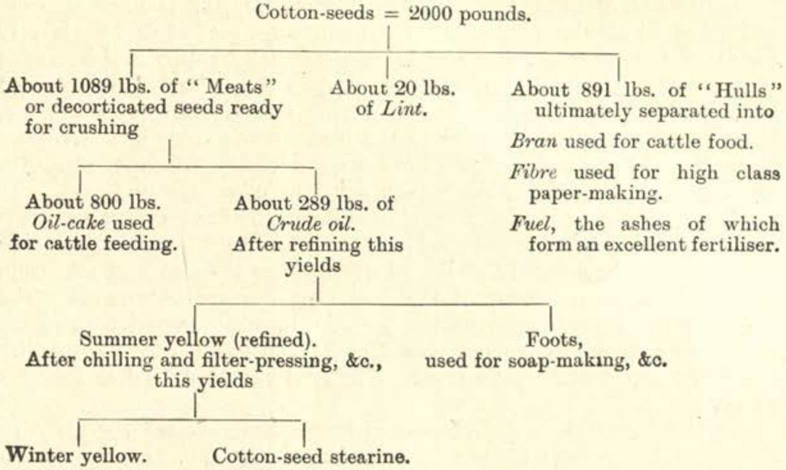
Waxes, on the other hand, are but little adapted for nutritive purposes. Thus beeswax (even when eaten along with honey) passes, for the most part, unchanged through the alimentary canal, and is not assimilated at all, either by human beings or other mammalia.

In the preparation for table and culinary use of oils and fats, etc., but little treatment of a technical nature is usually required, the chief points requiring attention being good quality of the raw material, and cleanliness in the treatment to which it is subjected. Thus the excellence of the butter prepared in a given dairy chiefly depends on the quality of the milk from which it is separated, and the care and cleanliness employed throughout the process. Very similar remarks apply to the preparation of the finer qualities of refined lard intended for food, and the ordinary kitchen operations of clarifying dripping, etc., and to the extraction of vegetable oils generally.

As already described, "virgin" oils, and "first runnings" are generally prepared from choice oil sources (olives, earth-nuts, etc.) by gentle pressure without heat, somewhat coarser grades being subsequently expressed by stronger pressure and heat combined; refining by agitation with water, subsidence, and straining, being usually preferred to processes involving chemical treatment.

In some parts of Russia and Eastern Europe much coarser oils are consumed by the peasantry than are usually similarly employed amongst either Western Nations or Asiatics; hemp-seed, poppy-seed, and linseed oils, often somewhat crudely extracted, being largely used as cooking oils. Of late years, however, sunflower-seed oil has to a great extent superseded these coarser oils; whilst in Western Europe, America, and many other parts of the world, cotton-seed oil, expressed by the hydraulic process described in Chap. x., and subsequently refined by boiling with alkalies, etc., is now very largely employed for many purposes for which formerly only olive oil was used, or the better grades of earth-nut oil, sesamé oil, and similar substances, the result of properly refining a fair quality of raw cotton-seed oil being to produce a light-coloured, pleasantly tasting, wholesome product, eminently well-adapted for frying fish and such-like cooking operations.

In connection with this the following table by *Grimshaw* is of interest, showing the way in which a ton of seeds is practically utilised :—



Cotton-seed Stearine (Vegetable Margarine).—When cotton-seed oil is chilled, a portion solidifies as solid glycerides; when these are separated by "bagging" or the use of a filter-press, and subsequently subjected to hydraulic pressure, a completely solid fat results. The more solid substances thus obtained are largely used as ingredients in artificial butter. The physical characters, and especially the melting point, vary somewhat with the extent to which the expression has been carried; usually cotton-seed stearine is pressed so as to melt at a little above 30°.

Among the Hindoos and others whose religious beliefs preclude the use of animal fats for edible and cooking purposes, there is now a large sale for purely vegetable fats of buttery consistence (vegetable lard). The process of semi-solid stearine extraction from vegetable oils (such as cotton-seed, coconut, and many other native oils) is consequently somewhat largely adopted for the purpose of meeting this demand, quite irrespective of the illegitimate use of these products for purely adulterative purposes in reference to more highly-priced animal fats, especially butter and lard.

Another substance, improperly called cotton-seed stearine, is obtained by distilling with superheated steam the mixture of organic acids formed when a mineral acid is made to decompose the " foots " obtained during the process of refining cotton-seed oil by alkalis (p. 347), and pressing out the " oleine " from the distillate after cooling and solidification. Products of this kind appear to contain a large amount of unsaturated solid fatty acids, possibly isoleic acid (p. 34). *A. H. Allen* found that a " stearine " of this kind had the specific gravity 0·868 at 99° C., and melted at 40° C., whilst the iodine value was 89·9; the theoretical value for pure isoleic (oleic) acid being 90·1. Other analytical data of cotton-seed stearine are given in Chap. XV.

Cultivation of Sunflower Seeds in Russia.—During the last two decades the oil obtained in Russia from sunflower seeds has very largely displaced the other cooking and table oils (chiefly poppy and hemp) in popular estimation, and the cultivation of the plant has increased enormously; with due care in the drying and cleaning of the seeds, the oil first expressed is equal to the best French table oils in colour, flavour, and taste. The shells form a considerable article of trade for heating purposes, whilst the stalks, dried in piles, are preferred even to pine wood for producing a quick and hot-flame fire; each acre yields about 2,000 lbs. of such firewood and some 1,350 lbs. of oil. The ashes contain much potash; 1,000 lbs. of dried stalks yield 57·2 of ash, from which about 35 per cent. of the best potashes are obtainable. The oil-cakes are looked upon as the best in Russia; superior to either hemp- or rape-seed cake; upwards of 2,000,000 lbs. are exported by the Government of Saratov alone. The seed cups are used as food for sheep.

In the larger mills the process of extraction is much the same as that used in England for linseed and rape-seed (Chap. XI.), the shelled seeds being dusted and crushed to a paste in a steam-heated vessel; the warm paste is wrapped in camel's hair webbing, and pressed. Out of 104 oil mills in Russia, 85 are employed solely in obtaining sunflower oil, steam being used in 24, and manual labour only in the others.[1]

Manufacture of Lard.—The fatty tissues of the hog when properly rendered furnish a white semi-solid grease considerably softer than the corresponding fat (tallow) from oxen and sheep, chiefly differing therefrom in containing more olein and less solid glycerides. In most of the larger American hog slaughtering factories the fats from different parts of the body are kept separate from one another, each being treated in a steam rendering pan reserved for that kind only; so that different grades are obtained of considerable constancy of character. The fat from the vicinity of the kidneys, and the " leaf " fat from underneath the skin furnish a superior and harder lard; whilst the fats from tainted carcases and diseased hogs, being generally melted down all together,

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[1] *J. Soc. Arts*, March 18, 1892.

produce the lowest grade. The finest qualities are usually put up in bladders, and the other sorts in kegs, whence the terms "bladder lard" and "keg lard" are respectively applied. Bladder lard, when pure, melts at 42° C. to 45° C.; keg lard at 28° C. to 38° C., according to its quality (*Allen*).

The particular texture exhibited by any given example depends largely on the way in which the cooling and solidification of the melted fat was effected, the texture being rendered firmer by stirring during solidification, or subsequent chilling in a refrigerating chamber. Sometimes water, salt, and a variety of other weight-giving adulterants (such as Iceland moss and starch) have been stirred in for the purpose of increasing the solidity of the mass. Sodium carbonate solution whitens the fat, and enables it to hold a larger proportion of water. The chief adulteration of American lard consists in subjecting the pure lard to pressure so as to express "lard oil," and then working up the residue with cotton-seed or other cheap oil so as ultimately to obtain a mass of the proper consistency and texture; beef suet, mutton tallow, and other fatty matters being often also introduced.

According to *Wiley*,[1] American lard was formerly classified under the following headings:—

(1) *Neutral lard*, consisting of fat obtained from the perfectly fresh leaf of the pig. This lard, which is rendered at a temperature of 105° to 120° F., contains only about 0·25 per cent. of free acid, and is used almost exclusively for oleomargarine.

(2) *Leaf lard*, consisting of fat from the unrendered residue from (1) subjected to steam heat under pressure.

(3) *Choice kettle-rendered lard—Choice lard.*—This is composed of the portions of leaf not used in (1), and of fat from the back rendered in steam-jacketed open kettles.

(4) *Prime steam lard*, obtained from the fat of the head, heart, and small intestines. It may practically represent the fat of the entire animal.

(5) *Guts*, which include everything inside the hog except the lungs and heart.

Other pig-fat products are known as:—

(*a*) *White grease.*—A fat rendered in tanks at a high temperature from animals dying in transit. It is obtained from the whole animal with the exception of the intestines which yield *brown grease*. It is used in the manufacture of soap and lard oil.

(*b*) *Yellow grease*, obtained from the refuse material of the packing houses.

(*c*) *Pigs'-foot grease* obtained as a bye-product in glue factories.

The Chicago Board of Trade classifies commercial qualities of lard as follows:—(*a*) *Neutral lard No. 1*, consisting of the leaf fat rendered below 50° C.; (*b*) *neutral lard No. 2*, obtained from the back fat; (*c*) *leaf lard*, obtained by digesting the residue from (*a*) with high-pressure steam; (*d*) *choice kettle-rendered lard*, obtained from the residue from

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[1] *U.S. Dept. of Agriculture. Bulletin*, No. 13. Part iv.

(*b*); and *prime steam lard*, prepared by digesting trimmings and fatty tissues from other parts of the animal with high-pressure steam. The intestines and viscera are used in the manufacture of *greases* of various grades.

Voigtländer[1] describes the difference between the American and German lards. Speaking generally, the former is harder and solidifies with a crystalline stellar formation after melting, whilst the German lard is much more fluid, and contains a larger proportion of the more unsaturated fatty acids. This difference is attributed by *Voigtländer* to the different kinds of food given to the pigs.

He states that American steam lard has a slightly burnt flavour, due to traces of burnt substances, to which must be attributed its superior keeping qualities.

Pure lard is steam lard rendered by the Hungarian process. The melted fat is mechanically stirred in closed vessels until solidification commences, when a certain proportion of solid lard is added. An addition of 5 to 8 per cent. of lard stearin is only made in the very best kinds. In *Voigtländer's* experience, steam lard thus refined will keep its consistency.

The differences in the analytical constants of European and American lards are described in Chap. XVI.—*Lard*.

When perfectly fresh, lard contains only minute quantities of free fatty acids, less than 1 per cent.; larger amounts are usually found in stale or partly rancid lard.

When chilled to 0° C. and pressed, lard furnished a solid stearine (sometimes known as *solar stearine*) and lard oil. The examination of the fluid oil thus obtained is often better adapted than that of the original lard for the purpose of detecting adulteration. Thus admixture of cotton-seed oil largely increases its iodine value, and interferes with the formation of a solid elaidin, and similarly in other cases.

Artificial Lard.—This name is sometimes applied to various mixtures of "beef stearine" (*vide infra*) and cotton-seed oil, or similar hard fats and vegetable oils, in such proportions as to give a product possessing the consistency of genuine lard. These substances are less frequently sold under names clearly indicating their nature than used for admixture in larger or smaller proportions with genuine lard for purposes of sophistication. According to some writers, adulterations of this kind are becoming much less common than they were a few years ago; but it is doubtful if any great improvement has really taken place in the trade, as a whole.

MANUFACTURE OF MARGARINE.

Mège Mouries Process.—The original *Mège Mouries* process, which was invented about 1869, consisted in treating chopped-up adipose tissue with a weak alkaline solution (potassium carbonate) and minced sheep's or hog's stomach at about 45° C., when partial digestion of the

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[1] *Zeit. angew. Chem.*, 1898, 857.

albuminous fatty envelopes and cellular tissue was brought about so that the fat separated, being "rendered" completely at the comparatively low temperature used. On cooling and standing, the solid glycerides separated more or less completely in a crystalline form, so that by applying pressure in cloths in an ordinary hydraulic press the still liquid portion was expressed, whilst a tolerably hard mixture of glycerides was left, valuable for candle-making.

Instead of the alkaline solution dilute hydrochloric acid was preferred by some, more especially with an addition of calcium phosphate, so as to form phosphoric acid or an acid phosphate of calcium; the digestive action was thus promoted and hastened.

Older Processes.—Until comparatively recently most of the margarine of commerce[1] has been prepared by processes analogous to that of Mège Mouries, excepting that the digestive operation is omitted. The sorted adipose tissue (carefully hand-picked, and sometimes washed to separate traces of blood and such like animal matters, and then finely minced) is subjected to gentle heat; in some cases alone, so that the constituents of lowest melting point drain off from the rest, the mass being supported in trays on sloping racks in a room kept at a temperature not much exceeding 50° C.; in other cases in tubs in contact with water at about 45° to 48° C., when the more fluid matters gradually rise to the surface and are withdrawn from time to time.

Beef suet is the preferable material, but sheep's fat is also employed; whilst much of the margarine made in America is derived from hog's fat, being in fact a variety of lard from which much of the solid matter has been removed. The partially exhausted tissues left are rendered in the usual way, either alone or mixed with other fatty matters, so as to produce a superior quality of tallow; the oleaginous fluid matters that result from the first processes are cooled and kept at about 25° C. for some time to allow the solid glycerides to crystallise, and the mass is then pressed.

The solid pressed residue is generally known as "beef stearine," and is largely used in the manufacture of artificial lard, being incorporated with cotton-seed or other fluid vegetable oil so as to form a mass of the required physical consistency.

The resulting expressed oil acquires a buttery consistence at the ordinary temperature, but is usually somewhat softer than cow's butter. By thoroughly churning it up with fresh (or, as preferred by some, sour) milk, and a little minced cow's udder, it acquires a slightly firmer consistence and a butter-like flavour. If the temperature during pressing has been too high, or if the solid glycerides have not sufficiently thoroughly separated whilst standing, the expressed substance may be too solid, in which case it is admixed with fluid vegetable oil (cotton-seed, earth-nut, sesamé, etc.).

The temperature at which the churning is effected has a good deal

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[1] The term "margarine" (μαργαρον or μαργαρίτης = pearl) derives its name from the *margarin*, the glyceride of Chevreul's "margaric acid" (see p. 22).

of influence on the physical character of the product; preferably the factitious "butter" is withdrawn and quickly chilled, either by running into ice cold water or on to slabs of solid ice, and then made up into "pats" for the market. Annatto, turmeric, saffron, and various other colouring matters (preferably vegetable, but sometimes of coal-tar origin) are used to communicate a yellow tint; sometimes a minute quantity of butyric ether or other special flavouring and odour-giving substance is added.

At the present day enormous quantities of solid vegetable fats, notably coconut oil and palm-kernel oil are used in the manufacture of margarine, and the vegetable preparation is to a large extent displacing the product made from animal fats as described above.

For example, in a trade report[1] it is stated that in 1911 Denmark produced 78,043,630 lbs. of margarine. Up to about 1908 the raw material consisted of about 70 per cent. of animal fat and 30 per cent. of vegetable oils, whereas, at the present time, the proportions have been reversed.

At one time, prior to the war, certain inferior grades of margarine contained a large proportion of stale butter, which had been churned up with milk, fresh fat, and flavouring reagent, but, at the present day, margarine rarely contains any butter, although the addition of 10 per cent. is permissible.

The following formulæ have been published[2] showing the composition of different grades of margarine manufactured in the United States prior to the introduction of hydrogenation processes.

HIGH GRADE MARGARINE.

	Parts.
Oleomargarine,	100
Neutral lard,	130
Butter,	95
Salt,	32
Colouring matter,	0·5
	357·5

Yielding about 352 parts of margarine.

MEDIUM HIGH GRADE MARGARINE.

	Parts.
Oleomargarine,	315
Neutral lard,	500
Cream,	280
Milk,	280
Salt,	120
Colouring matter,	1·5
	1,496·5

Yielding from 1,350 to 1,380 parts of margarine.

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[1] *Oil, Paint, and Drug Rep.*, Oct. 28, 1912.

[2] *Census Bulletin.*

CHEAP GRADE MARGARINE.

	Parts.
Oleo oil,	495
Neutral lard,	265
Cotton-seed oil,	315
Milk,	255
Salt,	120
Colouring matter,	1·25
	1,451·25

Yielding from 1,265 to 1,300 parts of margarine.

The introduction of the process of hardening oils by hydrogenation (see Chap. xv.) has rendered many oils available for the manufacture of margarine ; and the use of hydrogenated oils in place of oleomargarine has been claimed by *Dereaux* (Fr. Pat. 458,611 of 1913).[1]

In the United States manufacturers of " compound lard " now use cotton-seed oil hydrogenated to the desired extent, instead of their former mixtures of cotton-seed oil with 20 per cent. of oleostearine.

Attempts have been made to use hydrogenated whale and fish oils as constituents of margarine, more especially in Germany (see Chap. xv.), but in this country only vegetable oils and fats are used for the purpose.

Modern Processes of Manufacture.—With the advance in the scientific knowledge of the properties of colloidal solutions it was found that the emulsification of the fat with the milk could be effected perfectly by mechanical methods, without the use of the pepsin derived from the extracted cow's udder, on the mixture (*vide supra*), and many patents having this end in view have been taken out.

The Margarine Churn.—A common type of emulsifying machine is shown in Fig. 92, which is known as the *margarine churn.*

It is a cylindrical vessel in which agitators are made to rotate, whilst water or steam can be introduced through special inlets. The milk is introduced while the agitators are in motion, and after it has been brought to the desired temperature (preferably from 25° to 35° C.), the melted fat or mixture of fats is admitted gradually, and the whole agitated until the emulsion is formed.

At this stage cold water is introduced until the mixture has been cooled down nearly to the solidification point of the emulsion, and the whole contents of the churn are then run out to be cooled. In some types of the margarine churn the agitators are driven from below, but the principle of all is essentially the same. The drawbacks of this apparatus are that they require considerable power for driving in proportion to the amount of material treated, and that constant attention is necessary.

Schroeder's Emulsifier.—This is a distinct improvement on the margarine churn, the emulsifying vessel being much smaller (Eng.

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[1] *Oil, Paint, and Drug Rep.*, July 20, 1914.

Pat. 25,404, 1905). As shown in Fig. 93 the churning vessel, which is made to revolve at a high speed, contains two agitators, which beat

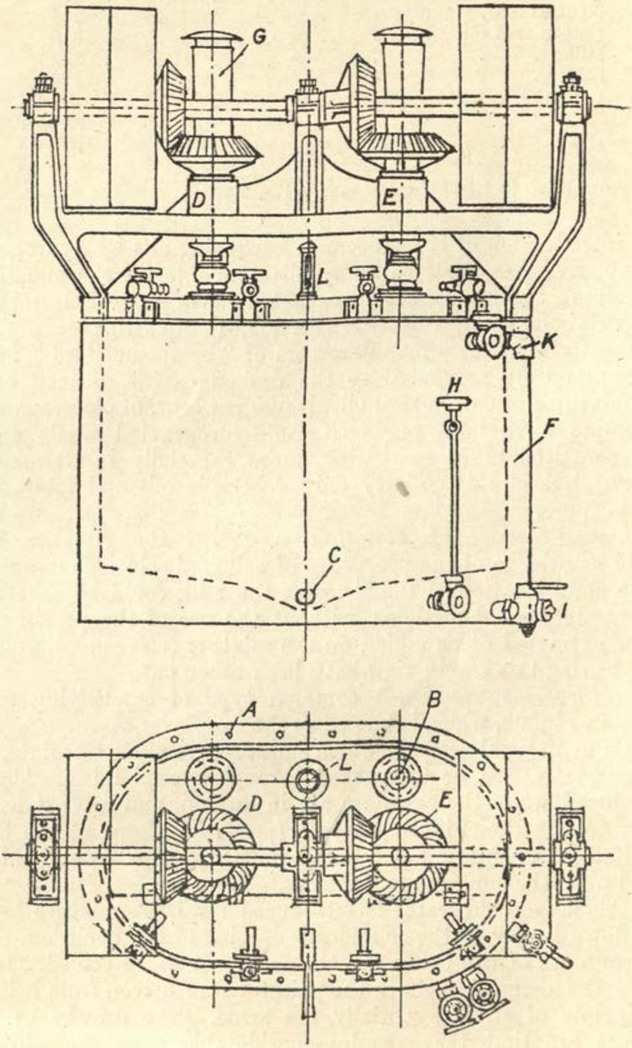
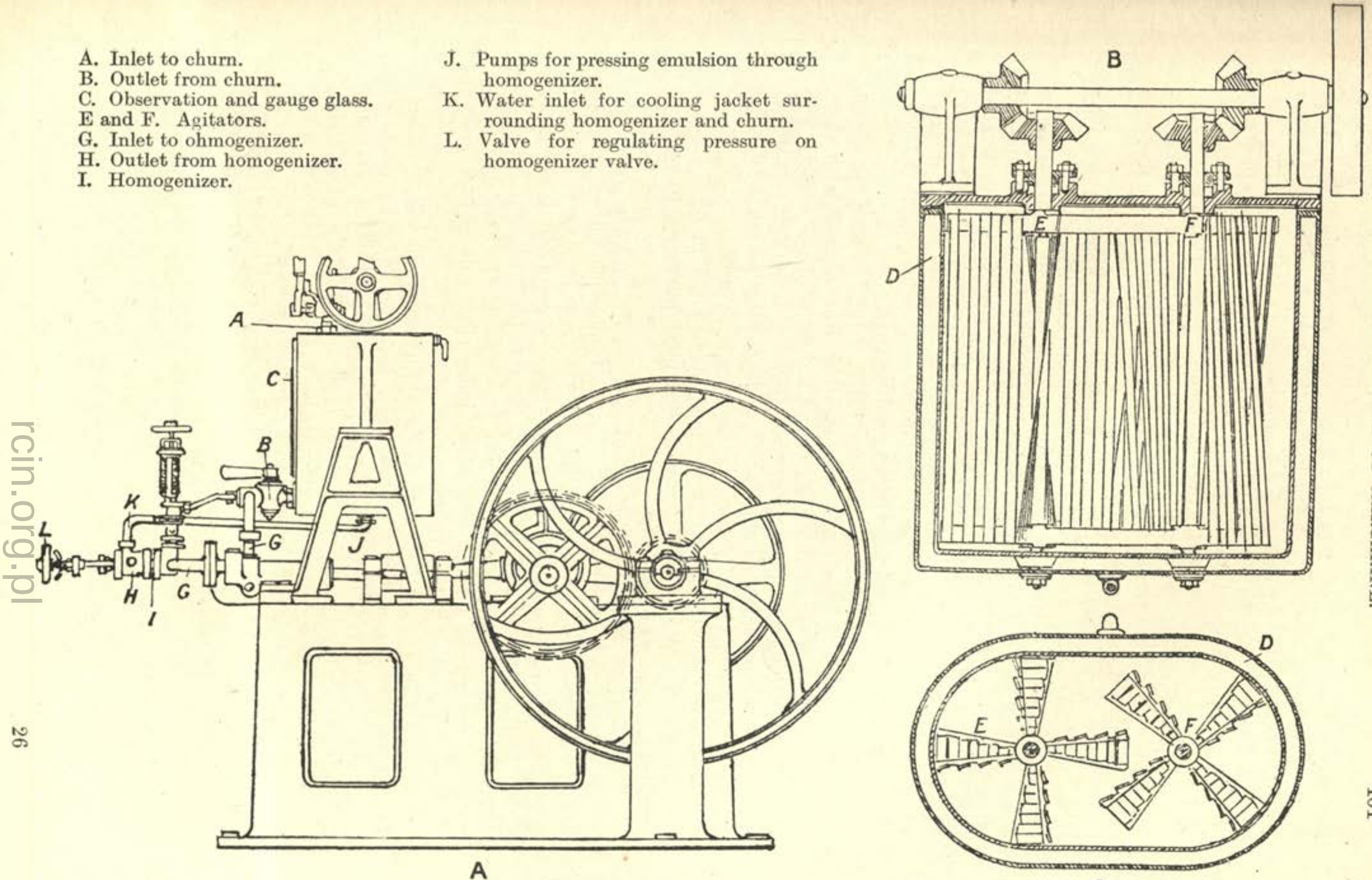


Fig. 92.—Margarine Churn.

A and B. Inlets for milk and fat blend.
C. Outlet for emulsion.
D and E. Drives for agitators.
F. Jacket for heating or cooling.
G. Ventilating pipes.
H. Valve for steam inlet.
I. Drain cock for heating jacket.
K. Overflow for steam.
L. Thermometer to indicate temperature of emulsion.



A. Inlet to churn.
B. Outlet from churn.
C. Observation and gauge glass.
E and F. Agitators.
G. Inlet to ohmogenizer.
H. Outlet from homogenizer.
I. Homogenizer.
J. Pumps for pressing emulsion through homogenizer.
K. Water inlet for cooling jacket surrounding homogenizer and churn.
L. Valve for regulating pressure on homogenizer valve.

Fig. 93.—Schroeder's Emulsifier.

the mixture of milk and fats into a fine creamy emulsion, and drive it to the bottom, whence it is discharged through an outlet. The temperature is regulated by means of a steam jacket.

After leaving the churn the emulsion passes through an apparatus where it is broken up still further into a fine homogeneous cream, which is discharged through an outlet into the cooling apparatus.

In some works several churns are used in association, and the cream-like emulsion leaving the last one is run directly into tubs for dispatch without going through any special cooling process.

Silkeborg's Emulsifier.—Another type of emulsifier devised by *Silkeborg* (Eng. Pat. 4,659, 1914) is shown in Fig. 94. This consists of a horizontal cylinder surrounded by a heating jacket and containing a shaft on which are several blades. As these rotate at a high speed they force the mixture of milk and fat against the surface of perforated baffle plates fixed between the blades. The holes in the successive baffle plates decrease in size, so that as the emulsion is driven through each series in turn it is broken up into finer globules, until it leaves the cylinder at the opposite end in the condition of a fine cream.

Blichfeldt's Emulsifier (Eng. Pat. 18,048, 1914) is another recent type of apparatus. This contains a rotating disc, pierced with slots, and mounted on a shaft which is close to the walls of the vessel. The milk or other fluid containing serum (*e.g.*, soya bean milk) is introduced into the vessel through the hollow shaft, while the melted fat is delivered from small openings in a tube which traverses the vessel.

Cooling the Emulsion.—After thorough emulsification of the blend of milk serum and fats it is necessary, for most purposes, to cool the product as rapidly as possible.

The processes used in this stage of the manufacture are commonly known as the wet or dry method. In the former ice water or, more usually, water chilled by refrigerating machinery, is used as the cooling medium. Thus, in one type of apparatus the emulsion leaving the churn is delivered in a thin film on to a sloping trough, where it encounters a current of water cooled to about 4° C., and falls as a solidified mass into a tank. Wooden blades then collect it from the surface of the water in this vessel.

Among the various types of cooling apparatus in which rollers, travelling bands, and the like are used, mention may be made of *Rasmussen's* cooler (Eng. Pat. 29,831, 1913). In this apparatus a hollow cylinder revolving in cold water receives a thin film of emulsion from the churn, and as the fat congeals it is removed from the surface by means of scrapers and deposited on a travelling band.

One drawback to this method of cooling the emulsion is that some of the milk proteins may be dissolved in the water, and the food value of the product thus reduced.

To obviate this, cooled skim milk or buttermilk is used in some factories as the cooling medium.

The wet process of cooling the emulsion is unsuitable for such fats as coconut oil and palm-kernel oil, which require very rapid chilling

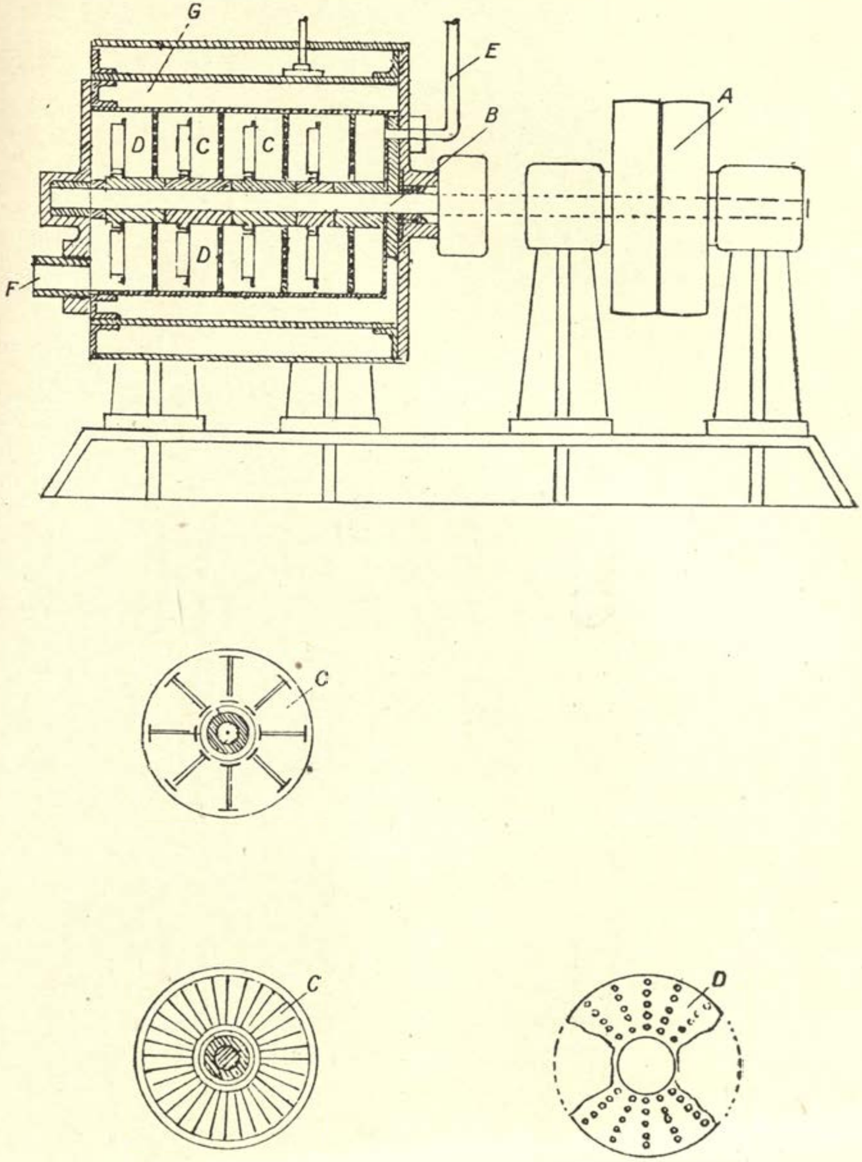


Fig. 94.—Silkeborg Emulsifier.

A. Pulleys for driving shaft.
B. Shaft on which mixers are keyed.
C. Mixers.
D. Perforated baffle plates.
E. Inlet.
F. Outlet.
G. Heating and cooling jacket.

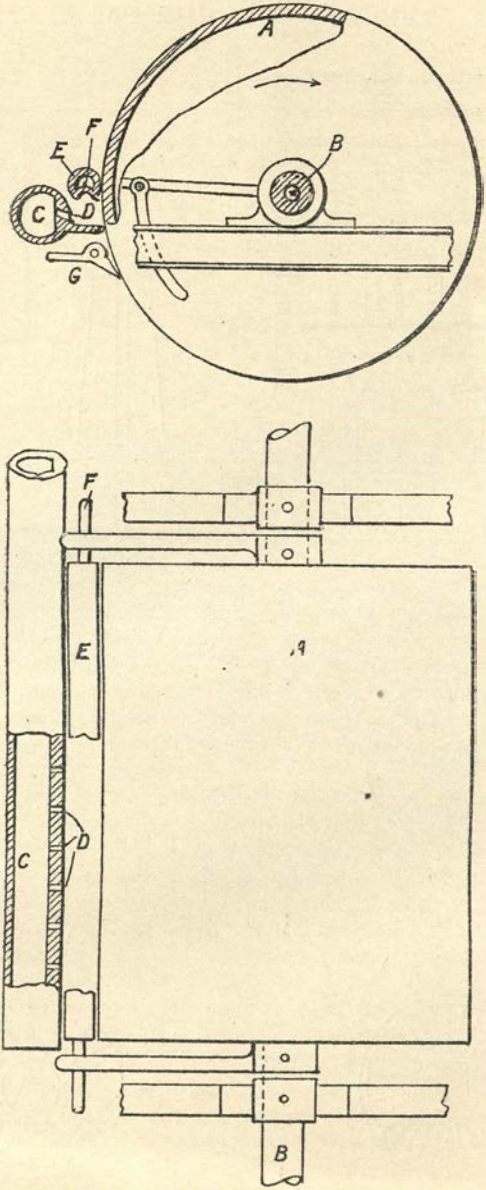


Fig. 95.—Christensen and Lauridsen's Cooling Drum.

A. Cooling cylinder.
B. Brine inlet.
C. Emulsion supply pipe.
D. Perforations to admit emulsion to cooling drum.
E. Regulator for thickness of layer.
F. Cavity for warm water circulating to avoid emulsion adhering to regulator.
G. Scraper knife.

to prevent them yielding a crystalline product. In such cases the use of chilled air gives better results, and various processes embodying this principle have been patented.

In one of these the emulsion leaving the churn is delivered on to a travelling band which passes through a casing and encounters a current of cold filtered air (Eng. Pat. 20,292, 1911). In one patent process (Eng. Pat. 17,613, 1913) the temperature of the emulsion is brought down to — 7° C.

Fig. 95 represents *Christensen* and *Lauridsen's* cooling apparatus (Eng. Pat. 20,568, 1912), in which the emulsion is distributed on to the surface of a rotating cylinder, through the interior of which circulates a current of chilled brine. The thickness of the deposit is regulated by means of a movable iron bar, and the material is removed from the surface of the cylinder by means of a fixed scraper.

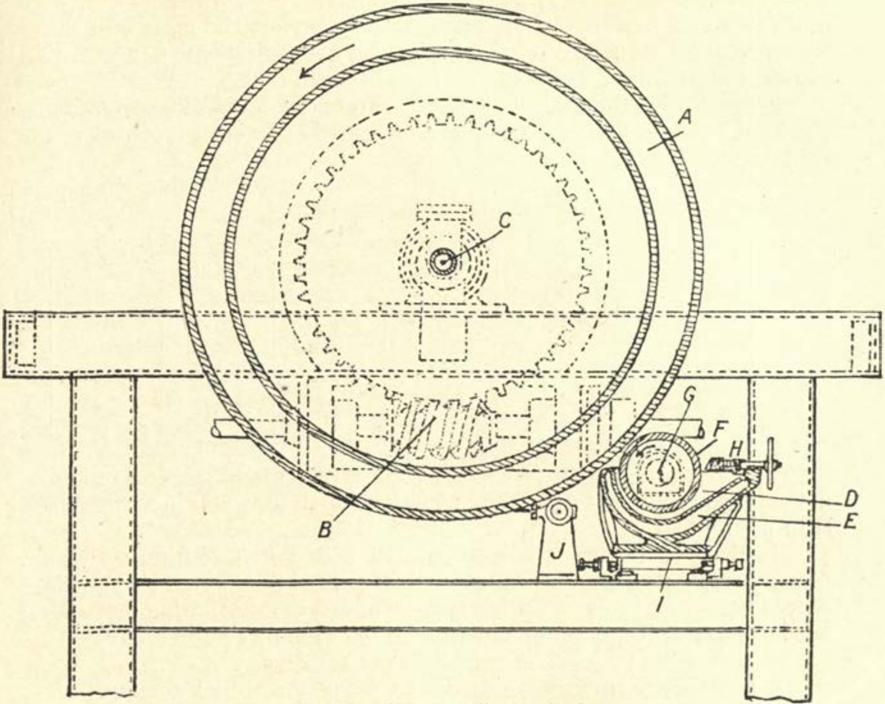


Fig. 96.—Jurgens' Cooling Drum.

A. Cooling drum.
B. Worm drive for same.
C. Brine inlet.
D. Trough for liquid emulsion.
E. Heating jacket for D.
F. Feeding cylinder.
G. Inlet for warm water to F.
H. Device for regulating thickness of layer on feeding cylinder.
I. Device for regulating distance between F and A.
J. Scraper knife.

In a similar form of apparatus devised by *Jurgens* (Eng. Pat. 10,863,

1914) a cylinder, through which circulates water at the same temperature as the emulsion, dips into the mixture as it revolves, and carries with it a certain quantity of the material, which it transfers to the cooling cylinder. This has a diameter about 8 to 10 times that of the feeding cylinder. It revolves in the same direction, and the thickness of the coating of emulsion is regulated by varying the speed of the small cylinder.

The addition of a small amount of gelatin or glycerin to the milk promotes the emulsification. After being cooled by one or other of these methods the so-called "crystals," are transferred to a special chamber, where the bacteria introduced with the milk are allowed to develop for some hours in order to mature the margarine. Then, in order to remove the excess of water, and to convert the mass into the consistency of butter, the matured "crystals" are subjected to a process of mechanical kneading, either in drums or between rollers.

Clayton [1] gives the analyses of two separate churnings of a margarine prepared by emulsifying 100 gallons of soured milk with 1 ton of oils containing animal fat.

The composition of the crystals before and after passing through a roller apparatus was as follows :—

	Fat, per cent.		Water, per cent.	
	(1)	(2)	(1)	(2)
Crystals,	67·30	67·30	27·46	27·47
Rolled product,	78·38	80·23	16·03	12·47

The average quantity of water in the crystals is 33 per cent., and in the rolled product 14·5 per cent. The legal limit for water in margarine is 16 per cent.

Finally, the margarine is incorporated with salt, colouring matter, preservative, etc., by means of "blenders," which are fitted with curved revolving blades. Butter may be added as a flavouring material not in excess of 10 per cent., and an addition of boric acid in an amount not exceeding 0·5 per cent. is usual as a preservative.

In some works means are taken to prevent material coming into contact with impure air throughout the entire process (*e.g.*, *Blichfeldt*, Eng. Pat. 4,508, 1912).

Production of "Browning" Properties.—Many of the patents in connection with the manufacture of margarine have for their object the production of an article which shall froth and turn brown like butter on heating.

In 1896 the Frankfurt Margarine Co. made use of yolk of egg for the purpose, and this addition was subsequently patented by *Bernegau*. Three years afterwards *Neisse* and *Boll* (Eng. Pat. 4,711, 1899) claimed

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[1] *J. Soc. Chem. Ind.*, 1917, xxxvi., 1208.

the use of egg-yolk formed into an emulsion with sugar, or with salt and sugar, and then added to the milk with which the fat is churned. According to *Mecke* the addition of sugar is superfluous, egg-yolk alone being sufficient for " browning."

In another patent (Eng. Pat. 21,626, 1900) *Neisse* and *Boll* describe a process of churning the egg-yolk with fresh milk or cream and sour milk, and incorporating the egg-butter with the margarine.

According to a German patent by *Backhaus* (1895) the fat is sprayed with finely-divided milk, and the same principle was embodied in *Uhlenbrock*'s patent (Eng. Pat. 8,194, 1896). Margarine thus prepared was stated to have a better flavour, and to keep better than the ordinary product; but, according to *Pollatschek*, this is not borne out by experience as regards the keeping qualities.

The addition of coconut milk was proposed in 1897; and in 1898 *Michaelis* patented in Germany the use of almond milk or other " vegetable milk containing emulsin."

Pellerini (Eng. Pat. 21,626, 1900) claims the addition of 0·5 to 5 per cent. of animal or vegetable wax as a " browning " agent.

Sterilised Margarine.—As the introduction of egg-yolk and other albuminous substances was found to impair the keeping qualities of the margarine, various attempts have been made to sterilise the ingredient and the finished product.

Thus in a process patented by *Dubuisson* (Eng. Pat. 4,489, 1895) the fat is sterilised by being passed through a coil heated to a temperature of at least 110° C., and is then cooled to 30° to 40° C.

In another process protected in Germany by the *Rhine Food Products Works* the margarine is prepared from sterilised fat and artificial sugar-free milk composed of sterilised ingredients. A typical artificial milk consists of the following substances:—Butter fat, 5 kilos.; proteid mixture (casein, 9 parts; albumin, 1 part), 1,250 grammes; 1 per cent. sodium hydroxide solution, 3,125 grammes; milk salts, 200 to 400 grammes; and sufficient water to make 100 litres. The price of this product is considerably higher than that of ordinary margarine.

Production of Butter Aroma.—In a process devised by *Scheffel* the fatty mass is treated with compressed air in a closed vessel, and the cooling is brought about by the expansion of the air. In this way all contact of the margarine with water is avoided, and a product with better flavour obtained.

An apparatus patented by *Theberath* and *Kunwald* (Eng. Pat. 22,018, 1894) has the same end in view. The oleomargarine and milk are forced into cylinders under pressure and incorporated by means of moving perforated discs at a temperature of 15° to 20° C. The mass is then forced into another cylinder, and rapidly cooled without contact with water.

Poppe (Eng. Pat. 18,500, 1898) employs a liquid cultivation of suitable bacilli (*e.g.*, *B. aromaticus*) instead of butter milk for the incorporation; whilst *Moppe* (Eng. Pat. 15,649, 1900) claims the use of a small addition of the liberated volatile fatty acids from pure butter.

Wilson (Eng. Pat. 24,051, 1911) uses a flavouring agent obtained by the action of bacteria on a mixture of casein and lactose in such proportion that no excess of either remains after the bacterial process. A similar bacterial process has been patented by *Schou* (Eng. Pat. 4,504, 1913).

Differences between Butter and Margarine.—The most important distinction between butter and margarine is that the latter shows a more or less marked increase in the Hehner value and a decrease in the Reichert value; whilst in many cases the specific gravity is slightly lower.

Margarine prepared from solid animal fats without admixture with coconut oil has a lower saponification value than genuine butter—viz., 192 to 199—and the iodine value is higher, usually ranging between 45 and 55.

But since methods have been discovered for removing the characteristic odour of coconut oil, the deodorised substance can be blended with the animal margarine in such fashion as to make the saponification and iodine values approximate closely to the figures given by genuine butter.

Moreover, since coconut oil and palm-kernel oil yield smaller proportions of insoluble fatty acids and more volatile fatty acids, their presence tends to lower the Hehner value and increase the Reichert value, thus rendering the detection of adulteration by these tests more difficult.

The methods of detecting foreign fats in butter are described under *Coconut Oil and Butter* in Chap. XVI.

"*Denaturing*" *of Margarine.*—With the object of enabling margarine to be readily distinguished from butter, and so preventing fraud, it has been proposed to make the addition of a small proportion of certain readily recognised substances compulsory, and in some countries these proposals have been in use for a considerable time.

Thus several years ago the Legislature of certain of the United States required margarine to be coloured pink, so that there should be no possibility of palming it off as butter.

Wauters came to the conclusion that the best substance to add was turmeric, and that at the same time the addition of that substance to butter should be forbidden.

As there are weighty objections against such methods the use of a "latent colouring matter" has met with more general support. For instance, if phenol-phthalein were added to margarine its presence would at once be indicated by the rose coloration produced on the addition of alkali. Similarly the addition of starch, as proposed by *Mainsbrecq*, would be indicated by the blue coloration given with iodine.

In *Partheil's*[1] opinion the most satisfactory substance for this purpose is dimethyl-amino-azobenzene, in the proportion of 1 per cent. This gives a rose colour on the addition of mineral acids, and being nearly insoluble in water cannot be washed out of the fat.

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[1] *Chem. Zeit.*, 1897, xxi., 255.

A few years ago the addition of 10 per cent. of sesamé oil to margarine was made compulsory by the German Government, after it had been shown that that oil could readily be identified by Baudouin's test (*q.v.*). This regulation, however, has not escaped criticism, for it has been pointed out by *von Raumer*[1] that many vegetable dyes give a coloration with hydrochloric acid alone, whilst turmeric gives practically the same colour as sesamé oil itself in the Baudouin test. He further regards this addition as unsuitable on the ground that it has been shown by *Spampani* and *Daddi*[2] that the milk of goats fed on sesamé oil gives the furfural reaction for that oil.

In considering the relative values of butter and margarine the question of the proportions of those medicinal substances associated with food, and known as *vitamines*, is of considerable importance. An outline of the present state of knowledge of these food constituents is given by *Ramsden*[3] who shows that whilst butter contains a large amount of one of these vitamines, margarine made from animal fats contains only half the quantity, and margarine from vegetable fats none at all.

Utilisation of Ox-Fat.—The table on next page, based on one given by Schädler,[4] represents the way in which the fatty matter from an ox is utilised.

FINAL PRODUCTS.

"Artificial butter" about 18 kilos., representing of oleomargarine	about	16·5	kilos.
Pure commercial "glycerine,"	,,	2·5	,,
"Stearine" (stearic and palmitic acids), . . .	,,	24·0	,,
"Oleine" (impure oleic acid), ...	,,	23·5	,,
"Scraps" used for manure, ...	,,	16·5	,,
		83·0	

It would hence seem that a very considerable loss of glycerol, accompanies the various processes gone through in the course of the isolation of the pure redistilled commercial article; for 24 kilos. of stearic acid, together with 23·5 of oleic acid, theoretically correspond with about 5·3 kilos. of glycerol instead of 2·5, indicating a total loss of more than 50 per cent. of the glycerol formed during saponification.

LAMP OILS.

From the earliest ages the use of lamps has been general essentially consisting of a vessel for holding the oil matter, provided with some kind of porous wick up which the oil rises, by capillary action, to supply the place of that burnt in the flame. Probably this arrangement was actually a development of the still earlier torch or

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[1] *Zeit. angew. Chem.*, 1897, 749.

[2] *Staz. sper. agric. ital.*, 1896, xxix.

[3] *J. Soc. Chem. Ind.*, 1918, xxxvii., 53.

[4] From results obtained in Sarg's factory, Vienna.

An ox yields about 83 kilogrammes of crude fat, from which are obtained, after careful separation of fleshy matters and impurities,

A
28 kilos. of so-called *kidney fat.*
After melting and pressing this yields

B
55 kilos. of *crude tallow.* After bleaching by treatment with steam in presence of sulphuric acid this yields

C
About 16·5 kilos. of so-called *oleomargarine.* After washing with water, and working up with milk, &c., this yields about 18 kilos. of "*artificial butter.*"

D
About 8·5 kilos. *stearine,* melting at 54° C.

E
About 3 kilos. *scraps.*

F
About 13·5 kilos. *scraps.*

G
About 41·5 kilos. *tallow,* melting at 45° C.

E and F together used as *butter.*

About 50 kilos. of D and G jointly yield, after saponification with lime and treatment with sulphuric acid,

H
Sweet water (dilute glycerol solution), from which are ultimately extracted by evaporation, filtration, distillation, &c., about 2·5 kilos. pure commercial "*glycerin.*"

I
About 47·5 kilos. of *crude fatty acids.*
After cold pressing these yield

J
About 32·5 kilos. of *cold press cake.*
After hot pressing this yields

K
About 15 kilos. of *red oils.* After chilling, crystallising, and filtering these yield

L
About 14 kilos *stearic acid.*

M
About 18·5 kilos. of so-called "returned acid" worked up again with fresh batch of I.

N
About 4 kilos. solid fatty acids worked up again with fresh batch of I.

O
About 11 kilos. *oleic acid.*

22·5 kilos. of M and N jointly ultimately yield

P
About 10 kilos *stearic acid.*

Q
About 12·5 kilos. *oleic acid.*

L and P jointly = about 24 kilos. *stearic acid.*

O and Q jointly = about 23·5 kilos. *oleic acid.*

flambeau, consisting in its simplest form of a splinter of pine containing natural resin, and in a more elaborate shape of strands of vegetable fibre dipped in resin, asphalt, and similar materials (obviously the prototype of the modern candle). The wicks used in some of the early forms of lamp appear to have been of rush-pith, apparently closely akin to the rush-candle or rush-light; saving that in the latter the vegetable wick was dipped in a comparatively solid fat melted by heat, and then taken out and allowed to harden, whilst in the former the wick was held in position by some simple device, and a thinner fat or oil used, fluid enough to moisten the wick without extraneous heat. In the modern "night-light" both forms are substantially combined, the arrangement being virtually a candle on first lighting, and practically an oil lamp after burning sufficiently long to melt the remainder of the fatty matter by the heat developed.

Amongst the Eastern nations, crude natural naphtha or petroleum has been largely used as a burning oil from time immemorial; but the methods now in use for purifying it and separating it into different fractions (some of which are far better adapted for burning in lamps than the raw material, whilst others are quite unfit for that purpose) are of quite modern origin. Amongst the Greeks and Romans, olive oil appears to have been largely used for the purpose; whilst rough candles of tallow, and superior ones of wax, were also in use. In all the early forms of household lamp no chimney was employed, so that the flame was invariably more or less smoky, a circumstance which considerably limited the number of vegetable oils available; in 1784, Argand introduced the form of lamp still bearing his name (although greatly altered and improved by subsequent inventors), essentially consisting of a circular wick with an air supply in the centre, a chimney of iron (later of glass) being also applied, so as to increase the draught and so facilitate combustion, thus diminishing smoke and increasing the light emitted.[1]

This invention greatly stimulated the use of oil lamps, and colza oil and sperm oil soon became extensively used for consumption therein, together with many other varieties, notably the oils from rape-seed, earth-nuts, and cotton-seed. At the present day, however, the use of these oils in this way, though by no means inconsiderable, is small as compared with that of the hydrocarbon oils from petroleum and paraffin shale, etc. (at any rate in those countries where the latter are readily obtainable), on account of the greater cost; but in many semi-civilised lands the cost of vegetable oils indigenous to the district is often below that of imported petroleum burning oils, so that the mineral oils have in such cases not yet largely supplanted the vegetable ones.

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[1] Flues or chimneys applied to lamps were not wholly unknown to the ancients; thus the lamp (of pure gold), designed by Callimachus about 400 B.C. for the Erechtheum of the Athens Acropolis, was provided with a chimney in the form of an inverted palm tree of bronze. Argand's use of a chimney was also previously suggested by Quinquet (Leopold Field, Cantor Lectures, *J. Soc. Arts*, 1883, 826 and 848).

When rape (colza) oil is burnt, a tendency to charring of the wick appears to exist if the oil contain much free fatty acids (formed by decomposition of the original glycerides during extraction and refining, etc.); this is also marked in the case of olive oil. According to *Archbutt*, 5 per cent. of free fatty acids is the maximum permissible, otherwise a defective light results, and the wick soon chars.

DRYING OILS USED FOR PAINT MANUFACTURE, AND IN THE PREPARATION OF VARNISHES, LINOLEUM, AND SUCH LIKE PRODUCTS.

Boiled Oils.—Drying oils, such as linseed oil, in their natural state as obtained by expression and refining (*raw* oils) absorb oxygen from the air and thicken at much lower rates than are observed after subjecting them to a form of treatment usually spoken of as "boiling," although the term is not strictly correct, inasmuch as the oils do not become converted into vapour capable of recondensation to the original substance as water or alcohol does when boiled, but only become partially decomposed so as to evolve vapours in consequence of incipient destructive distillation or other decomposition, more especially of the glyceridic portion of the molecule, whereby acrolein is formed.

In the older processes for preparing "boiled" oils, this effect was brought about by heat alone; subsequently various substances known as "driers" were added to the oil in small quantity for the purpose of promoting the particular changes in view. In the more modern methods somewhat lower temperatures are mostly employed, whilst the action is accelerated by injecting air into the hot mass, whereby a greater degree of incipient oxidation is effected, the result of which is to render the oil much more prone to oxidise spontaneously by subsequent exposure to air, and hence to "dry" more rapidly.

The nature of the driers used, and the exact methods of manipulation are often supposed to be valuable trade secrets; but the practical result of working secret "rule of thumb" methods of the kind has not always proved commercially successful. Some of the substances used under the name of "driers" (*e.g.*, dried alum and zinc sulphate) contribute but little, if anything at all, to the drying effect, their action being simply to coagulate remaining mucilage, and aid its subsequent removal by subsidence. Numerous metallic salts and oxides, etc., are, or have been, employed for the purpose; according to the experiments of *Livache*, the most marked effect in the way of increasing the rate of drying is produced by manganese and lead salts, copper, cobalt, and zinc compounds being much less active, and salts of iron, chromium, and nickel still less so. In actual practice, compounds of lead are those most frequently used, especially litharge, red lead, and lead acetate; the result of which is that the boiled oil finally obtained contains lead in solution as some kind of lead soap (to the formation of which, in the first instance, the action of improving drying qualities is probably due, the lead soap acting as carrier of oxygen); hence, more or less discoloration of paint made with such oil is apt to occur, especially in towns, independently of that brought about by the white lead added to most kinds of paint. This result is avoided by substituting manganese salts, etc., for lead compounds; accordingly, manganese hydroxide, dioxide, borate, oleate, oxalate, and other organic salts are now somewhat largely employed.[1]

When the drier is added in fine powder, a considerable fraction of it can be recovered, as it settles to the bottom when the oil is allowed to cool and stand; but a portion is taken into solution as metallic soap and permanently retained in the oil. Apparently this soap absorbs oxygen from the air, and then in some way parts with it again to the glycerides present; but the precise way in which the carrying action is effected is not thoroughly understood. In some cases, if too large a proportion of metallic soap is formed, the boiling oil produced is deteriorated, probably because the oxidising action then gets carried too far. By the use of the drier in the form of a solution of known strength, any required proportion can be readily introduced; manganese oleate or linolate, or other fatty acid manganese soap, dissolved in oil of turpentine or similar solvent, is accordingly coming into use for the purpose,[2] more especially for oils intended to mix with zinc white or other pigments of light tint where darkening is desired to be avoided, such as is liable to be produced in lead-containing oil by the action of sulphur compounds in the air. Moreover, oils "boiled" with manganese driers are generally of a lighter colour than when lead is used. Occasionally, to meet trade prejudices as regards colour, a mixture of lead and manganese compounds is used, so that the darker red tint produced by the lead may be developed to an extent proportionate to the quantity of lead employed.

The proportion of driers employed is usually but small, not exceeding 0·25 to 0·75 per cent. of the weight of the oil (a few lbs. per ton). When used in the solid form, it is important that they should be in the finest possible state of division, for which purpose they are usually subjected to a process of levigation after continued grinding. Finally, they are ground with oil, much as paint is ground, so as to form a mixture that can be readily disseminated through the mass of oil treated by means of agitators.

Apparatus.—In the older method of "boiling," the oil is simply heated along with the driers for some hours to a temperature varying

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[1] According to N. Clarke (*J. Soc. Arts*, February 10, 1893, 289), boiled oil prepared with manganese is unsuitable for varnish-making, as it produces a bloom on any varnish made with it.

[2] Hartley and Blenkinsop's process (Eng. Pat. 11,629, 1890) combines the drying action of manganese soap added in this form with the bleaching action produced by blowing a current of air through the mass at a temperature a little short of 100° C.; by using only a small proportion of manganese linolate solution, the oxidising action can be almost wholly confined to the colouring matter, so as to bleach the oil without producing any notable degree of other oxidation (*J. Soc. Arts, loc. cit. supra*).

from 200° to 250° C., free fire being used as the heating agent. Fig. 97 represents the kind of arrangement employed; a lid, *e*, is arranged, capable of being lowered on to the pan, *a*, and closing it up air-tight by means of the flanged rim, *b b*, so that in the event of the evolved vapours taking fire they can be almost instantaneously extinguished.

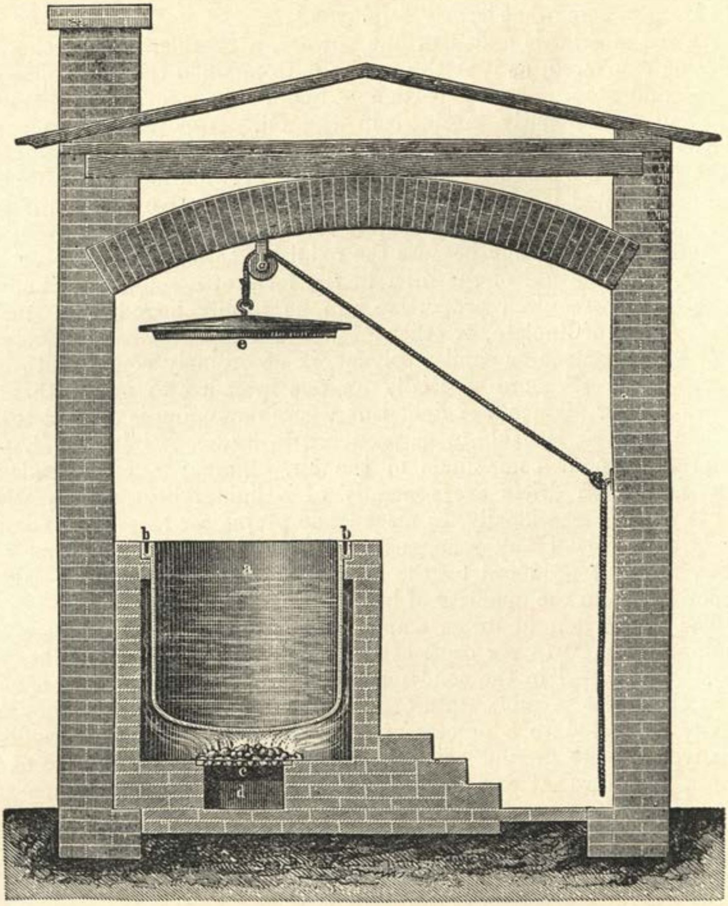

Fig 97.—Free-Fired Pan for Boiling Oil.

To avoid frothing over, the pan is originally filled not more than half full with oil.

Fig. 98 represents a pair of steam-heated kettles, the jackets being strong enough to resist several atmospheres' pressure; usually 4 to 5 atmospheres are employed, the oil being heated to 130° C. or a little upwards. When air is blown through the hot oil, a dome-shaped cover is fitted on to keep in splashes, provided with an exit pipe for the vapours evolved.

An improved vessel for boiling oil and suitable for many other kindred purposes was described by *Frederking*.[1] A coil of stout piping is arranged in a casting mould so that the molten metal forming the pan is cast round the oil; much as is done in the case of the water-tuyeres of a blast furnace. Steam at any required pressure being passed through the coil, the pan is heated up proportionately without any danger, the pressure bearing solely on the piping and not on the metal pan itself, whilst the well-conducting metal walls allow the heat to pass readily. Temperatures up to 350° and 400° C. can be thus obtained.

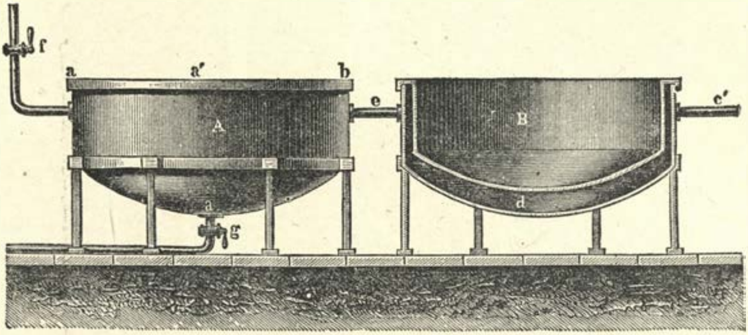

Fig. 98.—Steam-Heated Oil Kettles.

Fig. 99 represents a steam-jacketed mixing pan, which is suitable either for bleaching oils or for boiling linseed oil. It is provided with a mechanical agitator driven by means of the bevel gear wheel, *f*, and a pipe, *e*, ending in a blowing coil at the bottom of the vessel and connected with an air-pump, *a*.

According to *Vincent*,[2] the use of air alone without driers does nothing towards oil "drying." Linseed oil heated for three days consecutively at a high temperature in presence of the air but without driers required the same time to dry as the raw oil from which it was prepared, but the "body" was much increased. Heating alone for the same time with only surface exposure to air produced no such increase of body; the oil became more greasy, less penetrative, and less drying.

The exact nature of the changes taking place during the boiling of drying oils is not clearly understood; beyond the fact that an incipient alteration is produced (either by decomposition by heat, or by oxidation, or both together, largely assisted by the carrier action of the driers), which tends in the direction of the further changes effected

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[1] *Chemical News*, Jan. 27, 1893; German Pat. 63,315.

[2] Muspratt's *Dictionary of Chemistry*, edited by C. W. Vincent, ii., 475.

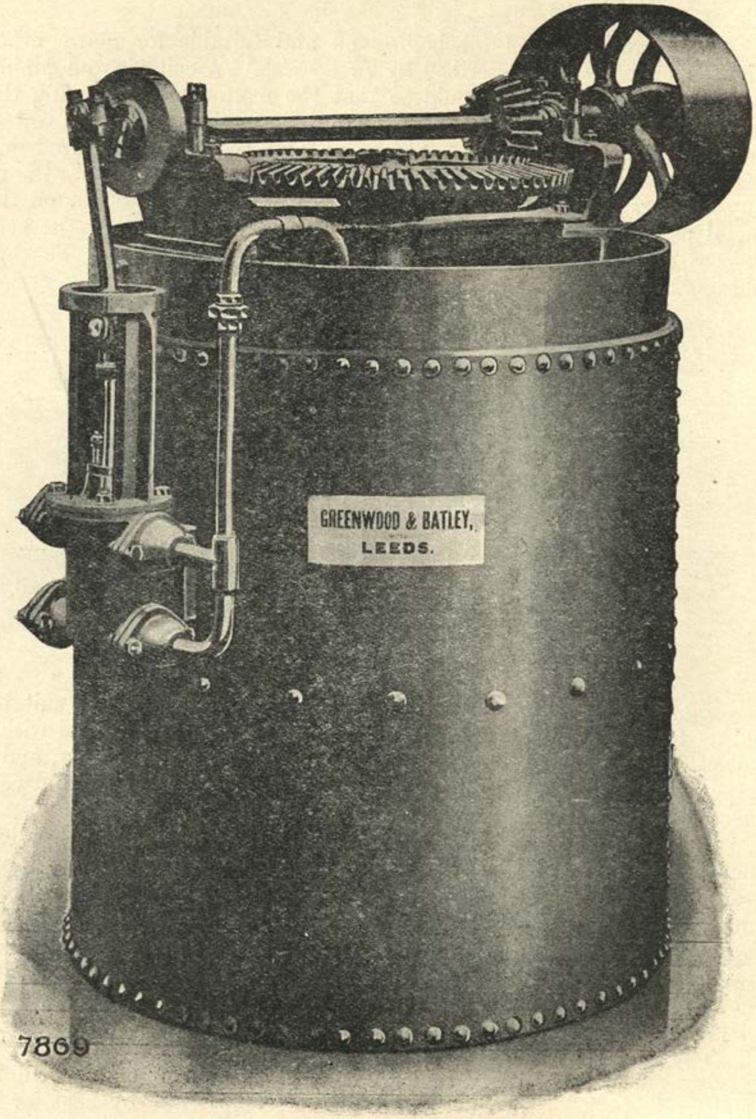

Fig. 99.—Steam Jacketed Heating Pan for Boiling Oils.

by the absorption of oxygen while drying, little is known with certainty. No considerable destruction of glycerides appears to occur until the action is pushed very far, ordinary "boiled" linseed oil furnishing nearly the same amount of glycerol on saponification as raw unboiled oil, so that the process appears to be mainly a polymerisation change; on the other hand, a more or less distinguishable small diminution in iodine-absorbing power is generally brought about indicating oxidation. For the further changes effected during actual "drying," see pp. 193-198, and for comparative analyses of raw and boiled linseed oil see Chap. XVI.

Printing Ink.—In the manufacture of printing ink, the action is pushed considerably further. In the older direct-firing process (still preferred by some) the oil is heated until the escaping vapours will fire freely; the mass thickens considerably as the action progresses; when a sample taken out and dropped on a cold porcelain surface can be drawn into strings half an inch long, a cover is put on to extinguish the flame; amber or rosin is then dissolved in the hot oil, and slices of soap (essential in order to enable the ink to adhere to damp paper); and finally the pigment (lamp black, ivory black, etc., mixed with Prussian blue or other coloured pigments to tone the black as required). Obviously in this case the heat causes a partial decomposition of the oil, and the thickening is probably due largely to an action of polymerisation taking place in the nascent acids or anhydrides thus formed, somewhat analogous to that which occurs during the "vulcanising" of oils by the action of sulphur chloride, etc. (p. 218).

A process of preparing printing ink from the alkaline mucilage deposited in refining cotton-seed oil has been patented by the *British Oil and Cake Mills* and *Wass* (Eng. Pat. 23,231, 1900). The deposit is mixed with acid tar, and the fatty acids liberated by the addition of mineral acid, dried, heated with resinous material, and incorporated with lamp black.[1]

Lithographic Varnish.[2]—This is frequently manufactured in the same way as boiled linseed oil, though at a considerably higher temperature (260° to 300° C.) and without the addition of "driers."

It is also prepared by subjecting linseed oil to the action of oxygen in steam-jacketed pans, and, as thus obtained, does not show the greenish fluorescence shown by the products obtained by heating over a fire.

"*Burnt Oil*" is the name given to a rapidly-drying varnish prepared by heating linseed oil until it takes fire, and then continually stirring it until a product of the thickness required is obtained.

Leeds (*loc. cit.*) gives the following analyses of lithographic varnishes prepared by these different methods, in which "*Fahrion's acids*" are the oxidised acids separated by the method described on p. 161:—

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[1] For further details of the manufacture and analysis of printing inks, see Mitchell and Hepworth's *Inks*.

[2] Leeds, *J. Soc. Chem. Ind.*, 1894, xiii., 203.

I. *Lithographic Varnishes. Boiled over Fire.*

Varnish.	Specific Gravity at 15° C.	Free Acids as Oleic Acid.	Saponification Value.	Unsaponifiable Matter.	Fahrion's Acids.	Iodine Value.
		Per cent.				
"Tint," . .	0·9584	1·46	197·5	...	1·50	113·2
"Thin," . .	0·9661	1·76	196·9	0·62	2·50	100·0
"Middle," .	0·9721	1·71	197·5	0·85	4·20	91·6
"Strong." . .	0·9741	2·16	190·9	0·79	6·50	86·7
"Extra strong,"	0·9780	2·51	188·9	0·91	7·50	83·5
"Burnt" thin, .	0·9675	6·93	195·5	1·35	0·85	92·7

Mixed Fatty Acids from "Boiled" Lithographic Varnishes.

Varnish.	Specific Gravity at 15° C.	Melting Point.	Solidifying Point.	Mean Combining Weight.	Saponification Value.	Iodine Value.
		° C.	° C.			
"Tint," . .	0·941	20·5	15	...	...	118·3
"Thin," . .	0·949	22	18	...	...	108·8
"Middle," .	0·950	24	22	272·6	205·8	97·7
"Strong," . .	0·953	25·5	24	270·1	207·7	87·3
"Extra strong,"	0·955	27	23	269·8	207·9	90·8
"Burnt" thin, .	...	23	19	...	...	99·3

II. *Varnishes prepared by Treatment with Oxygen.*

	Specific Gravity at 15° C.	Free Acid as Oleic Acid.	Saponification Value.	Unsaponifiable Matter.	Fahrion's Acids.	Iodine Value.
		Per cent.		Per cent.		
Oxidised oil, weak,	1·03	18-28·4	221	0·89	42·82	58·8
,, strong,	1·05	18·49-28·9	223·5	0·97	44·19	53·5
Dried linseed oil, .	...	12·67	171·6	0·81	31·58	93·9

Mixed Fatty Acids.

	Melting Point.	Solidifying Point.	Mean Combining Weight.	Saponification Value.	Iodine Value.
	° C.	° C.			
Oxidised oil, weak, . .	28	26	241·4	232·4	63·2
,, strong, . .	27	25	242·5	231·3	60·6
Dried linseed oil, . .	26	22	268·8	208·7	100·3

In the determination of the free acid in the above table, the first figure gives the result obtained by titrating the oil with phenol-phthalein as indicator, until the pink colour did not immediately disappear on shaking. After standing for some time, however, the colour disappeared, and more alkali was added until a final point (shown in the second figure) was again reached.

According to *Leeds*, oxidised varnishes are more soluble in alcohol, and dry more rapidly than the "boiled" varnishes. Being saturated with oxygen, they effervesce when heated.

Linoleum.—The varnish-like film of oxidised oil produced when boiled linseed oil is made to form a thin coating on a suitable large surface freely exposed to the air can be increased to an almost indefinite extent by painting a second film over the first when approaching dryness, and so on in succession. The product thus formed is largely employed in the manufacture of linoleum and floor-cloth, thin sheets of canvas or cotton scrim being suspended vertically in a room freely supplied with air, and "flooded" with oil from an overhead reservoir or tank running on wheels like a travelling crane. The sheets thus moistened with a film of oil are kept suspended with free access of air and when the coating is nearly dry, alternate floodings and exposure to air are repeated for some weeks until the "skin" formed is sufficiently thick, the chamber being supplied with warmed air if necessary, so as to keep its temperature up to at least 70° F. = 21° C., and freely ventilated, much acrid vapour (acrolein, etc.) being evolved during the oxidation by the destruction of the glyceridic portion of the oil.

The oxidised oil thus formed is heavier than water (raw linseed oil has the specific gravity 0·935 or thereabouts), and forms a yellow translucent mass, insoluble in alcohol, ether, chloroform, and carbon bisulphide; boiling naphtha (under pressure) softens it so that it can be worked into a paste. For the manufacture of linoleum the skins are ground between rollers, and heated with rosin and kauri gum in a mixing pan, and the resulting paste or "cement" then intermixed with rasped cork and ultimately spread upon a canvas backing.

Notwithstanding the loss of weight due to the evolution of acrolein and other volatile products during this process, a gain in weight averaging about 11 per cent. is experienced, so that the fixation of oxygen is considerable. In order to shorten the time requisite for the oxidation of drying oils for linoleum manufacture, *F. Walton* (Eng. Pat. 12,000, 1890) forces air at a pressure of 5 to 10 atmospheres through the oil warmed to about 100° F. = 37° C., the air current being divided by means of perforated plates; an agitator is provided, by means of which the product when approaching solidification is more or less granulated, whilst melted gums, etc., can be incorporated.

In a process protected by *Hertkorn* (Eng. Pat. 7,242, 1898) the oil is first boiled with or without the addition of an oxidising agent and alkaline earth. The resulting mass is mixed with finely-divided material —*e.g.*, powdered cork or sawdust, and oxidised by means of a current of air or oxygen. The elasticity of the product is increased by the addition of a hard resin powdered, whilst spontaneous ignition is prevented by the addition of oxides or soaps of alkaline earths.

The chief novelty in the apparatus is the mixing and oxidising cylinder, which is provided with a hollow shaft and hollow or perforated revolving wings, through which hot or cold air can be introduced.

Pinette [1] gives the following analyses of three samples of linoleum :—

		1.	2.	3.
		Per cent.	Per cent.	Per cent.
	Water, ...	3·39	3·01	3·41
	Linseed oil (ether-soluble),	10·43	10·60	19·58
	Cork (by difference), .	77·24	73·63	54·16
Ash,	Silica, ...	2·94	3·99	4·31
	Alumina, . . .	1·91	4·94	0·61
	Ferric oxide, . . .	1·78	1·79	8·86
	Calcium oxide, . .	...	...	6·17
	Alkalis, . . .	1·31	2·04	2·90

For further details of the development of the linoleum industry see *J. Soc. Chem. Ind.*, 1919, xxxviii, 26T.

Substitute for Boiled Oil.—Ammundsen (Eng. Pat. 9,828, 1901) prepares a substitute for boiled oil by mixing 100 parts of casein with 10 to 25 parts of a 10 per cent. solution of soap, adding 20 to 50 parts of slaked lime, and subsequently 25 to 40 parts of turpentine, and diluting the liquid with water to the consistency of boiled oil. This preparation is said to be a complete substitute for boiled linseed oil as a medium for paint, and colours so prepared can be applied to moist wood and brick walls.

Blown Oils.—Of late years the manufacture of oils oxidised by the direct action of air has acquired a considerable magnitude, the effect produced usually being a considerable increase in density and viscosity, rendering non-drying or semi-drying oils (rape, cotton-seed, fish oils, etc.) more suitable for use as lubricants, either directly or as ingredients in lubricating mixtures; and in the case of drying oils (more especially linseed oil), bringing about more rapidly and certainly those incipient oxidation changes necessary to produce more rapid spontaneous absorption of oxygen from the air by the oil, when spread out in thin layers—*i.e.*, the changes effected in so-called "boiled" oil, rendering it better applicable for the production of paint and varnish, etc., owing to its more rapidly "drying" up to a comparatively hard varnish-like coating when thus applied.

Weygang (Eng. Pat. 17,478, 1898) has protected a process of manufacturing siccative oils by treating mixtures of resins and petroleum with linseed or cotton-seed oil, "blowing" the mixture and thinning the final product with a suitable solvent.

The plant employed for the process is of simple construction, consisting of a pan or tank fitted with a steam jacket (or an internal dry

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[1] *J. Soc. Chem. Ind.*, 1892, xi., 550.

steam coil) for heating up the oil, and with a false bottom perforated with numerous small holes, cullender-fashion; air being pumped in under the false bottom rises up through the hot oil in numerous minute streams of bubbles. Instead of a false bottom, a horizontal serpentine with numerous pin holes is sometimes employed. When the action is intended to be carried to the limit, as in oxidising drying oils for linoleum-making, an agitating arrangement is also added for the purpose of breaking up clots, and keeping the mass well stirred up (*supra*).

Joselin (Eng. Pat. 1,397, 1901) agitates crude cotton-seed oil with an aqueous solution of a borate, and blows air through the purified oil kept at a suitable temperature.

The nature of the chemical changes taking place during the action of air on hot lard oil, cotton-seed oil, rape oil, etc., has not been thoroughly elucidated; a considerable amount of heat is developed during the process, so that, when once started, no further extraneous heating is necessary, but in some cases rather the converse, otherwise the temperature may rise so high as to injure the product by incipient decomposition. In all probability the olein present (or other homologous glyceride) becomes largely converted into the glyceride of an oxyoleic or oxystearic acid, either analogous to the ricinoleic acid of castor oil (*i.e.*, an unsaturated hydroxylated acid), or more probably constituted like anhydrodioxystearic acid (p. 50), where the oxygen is directly added on in the same way that iodine or bromine is added, so as to convert an unsaturated acid into a saturated derivative; for in proportion as the oxidation proceeds, the iodine absorption lessens. Other subsidiary reactions, however, also take place. Thus, the proportion of insoluble acids (Hehner value) lessens as the oxidation goes on, whilst increasing amounts of soluble acids are formed; the mean saponification equivalent of the blown oil is usually less than that of the original oil (*i.e.*, the "saponification value" increases), although but little increase is brought about in the "free acid value." Blown oils develop much more heat on mixing with sulphuric acid than the original untreated oils.

Commercial blown oils have usually nearly the same density and viscosity as castor oil, but differ from that oil in not dissolving freely in alcohol, whilst they are readily soluble in petroleum spirit, and mix readily with the heavier petroleum hydrocarbons, thus enabling homogeneous lubricating mixtures to be produced. Castor oil itself when similarly blown undergoes analogous changes, becoming still more viscid, and acquiring the property of being miscible with hydrocarbons (ordinary castor oil is almost insoluble in petroleum hydrocarbons, etc.); accordingly, blown castor oil is often spoken of as "soluble castor oil." The same term, however, is sometimes applied to the oil treated with sulphuric acid (Turkey red oil).

The following figures were obtained by *Thomson* and *Ballantyne*[1]

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[1] *J. Soc. Chem. Ind.*, 1892, xi., 506.

in the course of a series of experiments on the oxidation of rape and sperm oils by blowing hot air through them :—

Rape Oil.

	Original Oil.	Partly blown after 5 hours.	More fully blown after 20 hours.	Commercial Blown Rape Oil.
Specific gravity at 15·5° C., .	0·9141	0·9257	0·9615	0·9672
Percentage of free acid (calculated as oleic acid), . .	5·10	5·01	7·09	4·93
Percentage of unsaponifiable matter, ...	0·65	...	0·76	2·80
Saponification value, . .	173·9	183·0	194·9	197·7
Iodine value, ...	100·5	88·4	63·2	63·6
Specific temperature reaction,	135°	...	...	253°
Percentage of insoluble acids (Hehner value), . . .	94·76	...	85·94	82·40
Molecular weight of insoluble acids, ...	...	...	327	317
Percentage of soluble non-volatile acids, . . .	0·52	...	9·20	11·16
Percentage of soluble volatile acids, ...		...	0·82	1·90
Iodine value of soluble acids,	...	...	66·5	70·2

Sperm Oil.

	Before Blowing.	After blowing for 25 hours.
Specific gravity at 15·5° C., . . .	0·8799	0·8989
Free acid (calculated as oleic), . .	1·97	3·27
Unsaponifiable matter, ...	36·32	34·65
Saponification value, ...	130·4	142·3
Iodine value, ...	82·1	67·1

Distinction between Blown Rape and Cotton-seed Oils.—*Marcusson*[1] has devised a method of distinguishing between blown rape and cotton-seed oils when present in mineral lubricating oils. The fatty acids are separated from the oil and treated with petroleum spirit, and the soluble portion is converted into lead salts. On treating these with warm ether the lead salts from blown rape oil are practically soluble, whereas those from blown cotton-seed oil are only partially soluble. The insoluble lead salts amount to about 14 to 18 per cent. (calculated on the portion soluble in petroleum spirit) in the case of blown cotton-seed, fish, and bone oils, whereas a strongly oxidised linseed oil gave a value of 8 per cent.

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[1] *Mitt. K. K. Materialprüfungsamt*, 1911, xxix., 50.

Rosin in Blown Oils.—Fahrion[1] dissolves 5 grammes of the oil (freed from metals) in 50 c.c. of petroleum spirit, and treats the solution with 20 c.c. of 96 per cent. alcohol. After neutralisation with N-alkali the liquid is diluted to contain about 60 per cent. of alcohol, shaken and allowed to stand for 12 hours, after which it is diluted to over 200 c.c., acidified with hydrochloric acid, and extracted with two successive portions of petroleum spirit.

The united oils extracted are esterified with absolute alcohol, then rendered just alkaline to phenol-phthalein, diluted to an alcoholic strength of 60 per cent., and the rosin acids separated.

To compensate for errors in the method, amounts below 1 per cent. are ignored; amounts between 1 and 4 per cent. are taken as rosin; and those above 4 per cent. are multiplied by the factor 1·17, which corresponds with the amount (14 to 15 per cent.) of neutral substances and hydroxyabietic acid in colophony which escape estimation in the method.

Analyses of cotton-seed oil before and after "blowing" were given in Chap. VIII.

Oxygen Process.—A process was brought out under the auspices of "Brin's Oxygen Co." whereby commercially pure oxygen (containing 90 to 93 per cent. of actual oxygen) is used instead of air for the purpose of "boiling" linseed oil for varnish oil and linoleum, and similarly blowing other oxidisable oils, either in presence of a small quantity of driers, or without them (Eng. Pats. 12,652, 1886; and 18,628, 1889). In carrying out this process it was found unnecessary to blow the gas *through* the oil. A steam-jacketed pan was provided capable of being closed by a cover, and containing an agitator consisting of vertical rods or vanes moving round horizontally. When the oil to be treated had become heated nearly to 100° C., the agitator was set in motion, and oxygen introduced *above* the oil; the splashing oil drops presented a large absorbent surface, so that the oxygen was absorbed, at first comparatively slowly but later on with great vigour, so that although a rapid stream of gas was delivered into the pan it was absorbed more rapidly than supplied, producing a partial vacuum. As the action went on the oil became greatly heated, so that ultimately it became necessary to *cool* the jacket by admitting water into it. It was claimed that the oxidising action was under better control by this treatment, and that a superior result could be effected in a much shorter time, so that the extra cost of the oxygen gas was amply recouped.

A somewhat similar process was subsequently patented by *E. Opderbeck* (Eng. Pat. 24,153, 1892) for making "consistent fish fat, train, and other oils," by heating them to 90° to 100° C., and then bringing them into intimate contact with compressed oxygen.

In "blowing" oils with oxygen or ozone the oxidised product soon becomes insoluble in turpentine, and thus cannot be used for paint,

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[1] *Chem. Rev. Fett Ind.*, 1913, xx., 150.

etc. To obviate this *Banner* (Eng. Pat. 24,103, 1894) adds to the oil sufficient volatile solvent to keep it liquid.

An acceleration of the oxidation with ozonised air is said to be brought about by the addition of a small proportion of oxygen-consuming substance such as a hydrocarbon or tallow (*Andreoli*, Eng. Pat. 25,324, 1894). *Rosenblum* and *Rideal* (Eng. Pat. 9,529, 1897) have described an apparatus in which the oils, heated when necessary, are brought into contact with ozone under pressure and then sprayed into a covered vessel, where they meet a current of ozone. A mixture of equal parts of linseed and rape-seed oils is said to be solidified much more quickly than linseed oil by itself. The process is also suitable for the manufacture of cheap semi-solid products for linoleum and india-rubber substitutes. In a subsequent patent (Eng. Pat. 6,464, 1898) claim was made for the addition of driers to the oil oxidised by this process.

Conversion of Non-drying Oils into Drying Oils.—*Ramage* (Eng. Pat. 7,242, 1901) has devised a process of oxidising non-drying oils with the aid of an oxygen-occluding substance, such as metallic platinum. In a special apparatus described in the patent the oil is heated in a steam-jacketed vessel to about 200° C., then mixed with, say, 10 per cent. of platinised asbestos, and subjected to the action of ozone introduced through a perforated coil. After four to five hours the odour of the oil is destroyed and the specific gravity rises to 0·976; the product is then run off and filtered under pressure. It is stated to be practically a varnish drying on glass into a firm film, and requiring the addition of only a tenth of the quantity of resin to obtain the same results as given by ordinary drying oils.

MISCELLANEOUS USES OF OILS, FATS, ETC.

MANUFACTURE OF LUBRICANTS.

Nature and Uses of Lubricants.—The substances employed to diminish the friction between surfaces in motion relatively to one another are of very various kinds according to the nature of the mechanism, etc., to be lubricated. Thus for watches and chronometers on the one hand, and railway axles on the other, widely different substances are respectively most suitable; whilst the spindles of cotton spinning jennies, the piston boxes of steam engines, and the bearings of shafting generally, represent other different classes of moving objects for each of which special kinds of lubricants are required.

Formerly animal and vegetable oils and fats were almost exclusively used for lubricating purposes, the finer qualities being employed for the more delicate machinery and the coarser varieties and dirtier greases for the greasing of cartwheels and similar rough purposes; the introduction of railway travelling and the extended use of machinery of all kinds led to the modification of some of these materials by partial saponification with lime or alkalis so as to produce an imperfect soap containing much unsaponified fat, and to the admixture with them of more or less viscous hydrocarbons, more especially the "rosin oils" prepared by the distillation of rosin, and certain higher boiling fractions obtained in the treatment of petroleum shale oils, coal and other tars, and similar substances. At the present day "mineral oils" of this latter kind are most extensively used, either alone or in combination with saponifiable oils, although for certain special purposes the latter are still preferable. Obviously only those kinds of mineral oils are available that do not readily give off inflammable vapours, on account of risk of fire and the drying up of the lubricant by evaporation; moreover, lighter oils of this kind have not sufficient "body," especially for heavy machinery.

Of the animal oils, sperm oil stands pre-eminent, neat's foot oil, tallow, and lard oil being also valuable ingredients largely used, and to a less extent whale oil and various fish oils; whilst olive oil, palm oil, and rape oil, and to a less extent cotton-seed, sesamé, and earth-nut oils, etc., are also extensively employed.

In all such cases it is imperative that no free mineral acid should be present, as otherwise bearings, etc., are apt to be rapidly corroded: hence oils refined by acid processes (p. 345) are usually regarded as inadmissible as ingredients in first-class lubricating oils, unless the small quantities of admixed mineral acid have been thoroughly removed by a subsequent washing with an alkaline fluid.

There appears also to be good reason for regarding the presence of any considerable percentage of free organic acids as objectionable for similar reasons, more especially in the case of bearings made of gun-metal and other copper alloys, inasmuch as in presence of such acids the copper is apt to become oxidised, producing corrosion and pitting; hence oils refined by alkaline treatment are preferable. Cotton-seed oil thus refined (for the purpose of removing resin, Chap. XI.) owes much of its value to the circumstance that it is practically destitute of free acids, which to a great extent counterbalances the objection to its use that, as a considerable proportion of drying glycerides is present, it possesses a rather marked tendency to absorb oxygen and thicken or "gum" in use.

Animal and vegetable oils liable to contain free mineral acids, may be conveniently examined as to the presence of such constituents by the process described on p. 176; or the oil may be well shaken up with distilled water, and the aqueous liquor separated and examined, whilst the amount of free organic acids may be determined by the titration method described on p. 167.

A practical test as to the relative tendency to gumming is to place equal quantities (drops) of the oils to be examined on an inclined plane, noting the distance run down by each sample in a given time, and the time required before the oil ceases to run, owing to the increased viscidity through oxidation. Thus, the following figures are quoted from Appleton's *Dictionary of Mechanics*, representing the run of each oil in inches:—

	Sperm Oil.		Gallipoli (Olive) Oil.	Lard Oil.	Rape Oil.	Linseed Oil.
	Best.	Common.				
1st day, . .	32	19	10	10·25	14	17·5
2nd ,, . .	50	45	14	10·5	18	18
3rd ,, . .	53·5	55	18	10·75	19	18
4th ,, . .	54	59	18·5	10·75	19	18·25
5th ,, . .	54	62	19·5	11·75	19·25	18·5
6th ,, . .	54	64	20·5	Still.	19·25	Still
7th ,, . .	54	67	21	...	19·75	...
8th ,, . .	54	67·5	21·25	...	Still.	...
9th ,, . .	...	68	21·5	...	...	...

Only comparatively small amounts of unmixed animal and vegetable fats and oils are used alone at the present day as lubricants; a large proportion of the lubricating agents employed consist of hydrocarbons only, and the remainder are much more frequently mixtures of hydrocarbons, with saponifiable oils, than substances free from petroleum and rosin oils, and such like hydrocarbons.

One advantage gained in the case of such mixtures (apart from cheapness) is, that greasy rags, engine waste, etc., impregnated with oil, are much less likely to heat spontaneously through oxidation on storage (p. 186), when a large fraction of the oil is non-spontaneously oxidisable hydrocarbon, than would be the case were the oil wholly composed of glycerides and such like saponifiable bodies.

W. Brink finds (Eng. Pat. 17,163, 1889) that the solution of a small quantity of caoutchouc in a lubricating oil consisting of mineral hydrocarbons increases its viscosity and tends to prevent gumming, without introducing any corresponding disadvantages. Various metallic soaps, more especially aluminium oleate, are often added to lubricating oils for the purpose of increasing their "viscosity"; it is open to much question, however, whether such an addition really adds to the true lubricating power of the composition, and whether it should not be looked upon simply as an adulteration or falsification giving a fictitious appearance of consistency to the oil.

Jean[1] considers that a lubricating oil should have a fairly constant viscosity at 50° and 100° C., and that oils rendered viscous by the addition of soap should be prohibited.

Classification of Lubricants.—Lubricating materials other than pure fats and oils, may be conveniently classified in the following divisions:—

1. Solid, semi-solid, or more or less viscid liquid compositions of animal and vegetable oils and fats, with hydrocarbons from petroleum or destructive distillation (shale and paraffin oils), or resin oils containing little or no admixture of inorganic matters.

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[1] *Rev. Chim. Ind.*, 1897, viii., 193.

2. Solid or semi-solid greases containing a considerable proportion of saponaceous matters (alkali or lime soaps of fatty or resinous acids), together with more or less additional mineral or organic " anti-friction " substances (ground mica, steatite, plumbago, seaweed jelly, etc.).

3. Excessively coarse and generally dark-coloured greases, consisting of bye-products of various industries, the refining of which is too costly to permit of the materials being purified sufficiently to enable them to be utilised in other ways—*e.g.*, " Yorkshire grease," and grease from engine waste (p. 321), containing too much hydrocarbons, etc., to be worth distilling for so-called " stearine " and " oleine " (p. 343); " dead oils " obtained in coal-tar distillation; certain kinds of " foots " obtained in refining; pitchy and tarry matters of various kinds not available for other purposes, and so on.

Lubricants of the first class include " engine oils," " engine tallow," and similar compositions; " cylinder oils " for lubricating the piston rods, etc., of steam engines; " machinery oils " for shafting, bearings, crank axles, and the like; " spindle oils " for quick-moving light machinery, like the spindles of cotton spinning jennies; watchmakers', clock, and " turret " oils, specially adapted for delicate machinery like chronometers, and not liable to thicken by cold—and a large variety of subordinate kinds. Those of the second class are chiefly compositions used for the axle boxes of locomotive stock (railway trucks and carriages, etc.). Coarse greases of the third class are used for cartwheels and rough machinery, such as the pumping engines employed in mining, where, through the circumstances of the case, high-class lubricants are unnecessary.

Lubricants of the First Class—Lubricating Oils.—The examination as to the practical lubricating value of materials and compositions of this class is rather a mechanical than a chemical problem. A laboratory test greatly relied on as an indication of their suitability for the particular purposes in view, is the determination of their relative efflux rates at given temperatures. The so-called " viscosity " values thus obtained by means of one or other of the various forms of efflux viscosimeter described in Chap. v. (or better still, the figures obtained by means of appropriate large scale testing machines, etc., whereby the conditions obtaining during actual use can be nearly imitated) are generally of more practical value to the consumer than chemical analyses of the substances; especially when coupled with valuations of the flash point (p. 178) and the degree of volatility—*i.e.*, the rate of loss by volatilisation on heating to known temperatures. On the Continent considerable stress is often laid on the determination of the " congealing point " (*vide* p. 89). For an outline of the standard methods and appliances which have been used for the purpose, *vide J. Soc. Chem. Ind.*, 1890, ix., 772.

Lant Carpenter summarises the general experience gained as to the character and behaviour of the various oils used for lubricating as follows :—

1. A mineral oil flashing below 300° F (149° C.) is unsafe on account of causing fire.

2. A mineral oil evaporating more than 5 per cent. in ten hours, at 140° F. (60° C.) is inadmissible, as the evaporation creates a viscous residue, or leaves the bearing dry.

3. The most fluid oil that will remain in its place, fulfilling all other conditions, is the best for all light bearings at high speeds.

4. The best oil is that which has the greatest adhesion to metallic surfaces, and the least cohesion in its own particles; in this respect fine mineral oils are 1st, sperm oil 2nd, neat's foot oil 3rd, and lard oil 4th.

5. Consequently, the finest mineral oils are best for light bearings and high velocities.

6. The best mineral oil to give "body" to fine mineral oils is sperm oil.

7. Lard and neat's foot oil may replace sperm oil when greater tenacity is required.

8. The best mineral oil for cylinders is one having specific gravity 0·893 at 60° F. (15·5° C.), evaporating point 550° F. (288° C.), and flashing point 680° F. (360° C.).

9. The best mineral oil for heavy machinery has specific gravity 0·880 at 60° F. (15·5° C.), evaporating point 443° F. (229° C.), and flashing point 518° F. (269° C.).

10. The best mineral oil for light bearings and high velocities has specific gravity 0·871 at 60° F. (15·5° C.), evaporating point 424° F. (218° C.), and flashing point 505° F. (262° C.).

11. Mineral oils alone are not suited for the heaviest machinery on account of want of "body" and higher degree of inflammability.

12. Well purified animal oils are applicable to very heavy machinery.

13. Olive oil is foremost amongst vegetable oils, as it can be purified without the aid of mineral acids.

14. The other vegetable oils admissible, but far inferior, stated in their order of merit, are gingelly, earth-nut, colza, and cotton-seed oils.

15. No oil is admissible which has been purified by means of mineral acids.

A. H. Allen regards the following characters as those which should be taken into consideration in forming an opinion as to the suitability of a lubricating oil for a given class of work:—

1. The *viscosity* or "body" of the oil at the temperature at which it is to be used.

2. The temperature at which the oil *thickens* or actually *solidifies*.

3. The *flash point* or temperature at which the oil gives off inflammable vapours in notable quantity.

4. The *volatility* or loss in weight which the oil suffers on exposure in a thin film to an elevated temperature.

5. The "gumming" character or tendency of the oil to become *oxidised*.

6. The relative proportions in which the *fatty* and *hydrocarbon oils* of a mixture are present.

7. The proportion and nature of the *free acid*, if any, in the oil.

8. The tendency of the oil to act on metals.

9. The presence of *mineral matters*, such as the metallic bases of soaps, etc.

Action of Lubricating Oils on Metals.—Aisinmann[1] made a series of experiments to obtain data as to the permissible amount of acid in mineral lubricating oils, and from his results came to the conclusion that the limit allowed by the German State Railways (0·1 to 0·3 per cent.) might be exceeded without risk in the case of cold-running machinery.

As regards the action of fatty oils on metals *Donath*[2] concludes that their corrosive influence depends to a large extent on whether the oiled surface comes in contact with atmospheric oxygen, and whether by any means water gets into the oil. He finds that fats and fatty acids have no direct chemical action in themselves upon metals.

Friction at High Temperatures.—*Kapff*[3] opposes the view of Thurston, who concluded that the coefficient of friction of an oil decreased with the rise in temperature to about 82° C., and that heating of the bearings to that temperature was harmless. In Kapff's opinion heating of bearings to 80° C. points to the use of too little oil or to the presence of dirt. He regards the following as desiderata of a good lubricating oil:—(1) The oil should be free from acid and solid particles, and should not resinify or develop acidity on exposure; (2) it should have good adhesive qualities; and (3) it should offer small frictional resistance at the temperature of use.

As regards the degree of volatility of a lubricating oil, *J. Carter Bell* considers that it would be well for insurance companies to lay down a hard and fast rule that no lubricating oil should be used in any mill that has a flashing point lower than 350° F. (177° C.), and that loses more than 5 per cent. in twelve hours at 140° F. (60° C.).

Lubricants of the Second Class—Carriage and Waggon Greases.—For the axle boxes of railway rolling stock a peculiar kind of imperfect soap is found to answer well, usually made by melting tallow and palm oil together, and then thoroughly incorporating a solution of sodium carbonate in water, for which purpose Morfit's steam twirl (Chap. XIX.) answers well; or a boiled palm oil soap is dissolved in hot water and thoroughly intermixed with melted tallow, the emulsified mass being then cooled so as to solidify.

Richardson and Watts[4] give the following formulæ for compositions

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[1] *Zeit. angew. Chem.*, 1895, 313.

[2] *Dingler's polyt. J.*, 1895, ccxciv., 186.

[3] Abst. *J. Soc. Chem. Ind.*, 1901, xx., 1222.

[4] *Chemistry applied to the Arts and Manufactures*, vol. i., part iii., 744.

of this kind that have been used with excellent results, that marked "summer" running for 1,200 miles :—

	Winter.					Summer.				
	Cwts.	qrs.	lbs.		Lbs.	Cwts.	qrs.	lbs.		Lbs.
Tallow,	3	3	0	=	420	4	2	0	=	504
Palm oil,	2	2	0	=	280	2	2	0	=	280
Sperm oil,	0	1	7	=	35	0	0	27	=	27
Soda crystals,	1	0	14	=	126	1	0	8	=	120
Water,	12	3	12	=	1,440	12	0	26	=	1,370
	20	2	5		2,301	20	2	5		2,301

These quantities are reckoned to give 1 ton = 2,240 lbs. of grease, allowing about 2½ per cent. for loss.

Allen gives the following composition of a similar German waggon grease :—

Tallow,	24·6
Palm oil,	9·8
Rape oil,	1·1
Caustic soda,	5·2
Water,	59·3
	100·0

The following composition, containing a smaller proportion of saponaceous matter, has been patented by *Hervieux* and *Bedard* (Eng. Pat. 4,190, 1889) as a superior form of axle grease :—

Codfish oil,	24 parts.
Beef tallow,	16 ,,
Rosin,	1 ,,
Soft soap,	2 ,,

A somewhat analogous imperfect lime resin soap is used for railway trucks unprovided with axle boxes, carts, and waggons, and similar vehicles. This is made by elutriating slaked lime (by stirring up with water and running the "milk of lime" through a succession of settling tanks), and thoroughly intermixing the lime-mud with rosin oil in the cold. The resulting mass is often intermixed with coarse greases and other substances of the third class, and sometimes with mineral substances possessed of anti-frictional qualities.

Thus, the following composition has been patented by *A. Purvis* (Eng. Pat. 13,936, 1890) as an improved lubricant capable of resisting unusually high temperatures :—

Japanese tallow,	2 cwts.
Russian tallow,	3 ,,
Olive soft soap,	2 ,,
Lard oil,	108 lbs.
Castor oil,	108 ,,
Calcium carbonate,	10 ,,
Sodium carbonate,	10 ,,

The mass is heated and well intermixed, with the addition of ½ cwt. of finely-pulverised mica, or of china clay, or of the two together. After standing twenty-four hours it is again heated, and 20 lbs. of zinc oxide added; after thoroughly commingling, the mass is then subjected to hydraulic pressure so as to squeeze out any water present.

Numerous analogous mixtures, consisting essentially of tallow or oil, soap of some kind, and solid powdery matter (such as graphite, steatite, or sulphur) are in use as anti-friction compositions.

Greases of the Third Class.—These are the most dangerous lubricating materials in use from the point of view of liability to inflammation; refuse coal-tar dead oils, anthracene oils, creosote oils, etc., have frequently a relatively very low flash point, and when once set on fire are not easily extinguished. Such compounds should not be used at all in a mill or similar building where great damage by fire might be occasioned.

Analysis of Lubricating Oils and Greases.—Oils, etc., consisting wholly of organic matters will obviously leave no ash on careful incineration, whereas, if any soapy material or other inorganic "anti-friction" constituent be present, more or less residue will be left when a known weight of substance is cautiously heated (*e.g.*, in a platinum dish) and the residual carbon burnt off. An examination of this residue may be made as regards the quantity of alkali contained, the amount of lime, alumina, steatite, etc., present, and so on.

Organic suspended matters, such as Irish moss or seaweed jelly, lime, or other soaps insoluble in ether or petroleum spirit, etc., may be conveniently sought for by thinning the material with the solvent, and passing through a weighed filter, finally washing out all soluble matters; the residue may be weighed, a portion incinerated to obtain the proportion of inorganic matters present, and the remainder further examined as may seem requisite. When metallic soaps (alumina, iron, etc.) are present, the metallic basis can be conveniently removed by thinning the grease with ether, etc., and agitating with water strongly acidulated with hydrochloric acid.

When saponaceous matters are present (*e.g.*, when the "foots" from oil-refining by alkaline processes are used as ingredients, or when lime and rosin spirit, or soda and palm oil, etc., are used, as with certain kinds of waggon grease), the methods employed in soap analysis are available with suitable modifications. Thus, the total alkali present may be conveniently found by shaking with ether and a slight excess of standard acid (hydrochloric or nitric), separating the aqueous part and titrating the excess of acid not neutralised. By adding phenolphthalein to an alcoholic solution of the oil or grease, and cautiously dropping in standard acid, and shaking after each addition, the amount of alkali or alkaline earth present otherwise than as soap may be at least approximately determined; and by further diluting with water, adding ether, petroleum spirit, carbon bisulphide, or other convenient solvent, and excess of standard acid, the total alkali, etc., may be determined as above; whilst, after separating the solution of oil in ether, etc., the fatty and resinous acids set free may be titrated in the usual way (p. 166).

Glycerides (animal and vegetable oils and fats) and liquid waxes (sperm oil, etc.) are determined as in the case of ordinary oils. After neutralisation of free fatty acids (or alkalis) excess of standard alkali is added with alcohol, the whole boiled some time under a reflux condenser and the alkali not neutralised determined. The product diluted with water and shaken with petroleum spirit gives an aqueous solution of the soap formed by saponification of the glyceride, from which the contained fatty acid may be separated and subjected to examination; whilst the petroleum spirit contains in solution the hydrocarbons present in the original grease, together with non-fatty acid oxidised matters, such as cholesterol from wool-grease, etc., the higher alcohols formed by saponification of sperm oil, and the like. These may be further examined by the acetylation process (p. 265).

As a general rule, the chemical analysis of a given lubricant affords very little information as to its suitability for any particular purpose; but certain laboratory determinations are often of considerable value, more especially the determination of rate of loss of weight on heating to given temperatures for specified times; of the efflux "viscosity" at specified temperatures; and to a less extent of the specific gravity. The "flash point" and the somewhat higher temperature of firing ("ignition point") are also important, especially with mineral oils. The principal chemical tests of practical value are those for free mineral and organic acids, more especially the former. The chief utility of analysis in the case of lubricating oils is to decide whether they are of the composition stipulated for in a contract—*e.g.*, as to containing a given percentage of sperm oil intermixed with hydrocarbons, and so on; or to see whether otherwise genuine—*e.g.*, in the case of rape or castor oil, as to whether adulterated with other substances, such as cheaper oils or hydrocarbons; or in the case of blown oils, whether artificially thickened by addition of soft soap, aluminium oleate, rosin, and so on.

Occasionally it is required to find out whether rosin oils have been admixed with mineral oil lubricants; for this purpose the glacial acetic test described on p. 74 may be conveniently used, rosin oils being readily soluble, whilst mineral oils are practically insoluble in that solvent.

Rate of Absorption of Oxygen.—According to *O. Bach*, the facility with which a lubricating oil absorbs free oxygen is a useful measure of its "gumming" tendency. By sealing up in a glass tube containing 100 to 125 c.c., quantities of oil of from 3 to 5 c.c., after displacing all air by oxygen, and heating for ten hours to 110° C., a more or less considerable absorption of gas takes place, which can be readily determined by opening the sealed-up end of the tube under water, and noting the decrease in the volume of gas. Thus various kinds of oils gave the following numbers :—

1 gramme of	Valve oil (mineral)	absorbed	0·1	c.c. of oxygen.
,,	Valveoline	,,	0·45	,,
,,	Lubricating oil	,,	0·7	,,
,,	Oleonaphtha	,,	8·6	,,
,,	so-called " Cod oil : sp. gr., 0·963	,,	76·3	,,
,,	Olive oil	,,	144·0	,,
,,	Rape-seed oil	,,	166·0	,,
,,	Cotton-seed oil	,,	171·0	,,
,,	Rosin oil	,,	181·0	,,

In the case of mineral oils little or no acidity is shown by the water sucked in, but in others with which the absorption of oxygen is large, a strong acid reaction is manifest, especially in the case of rosin oil.

TURKEY RED OILS.

The chemical differences between the two kinds of oils treated with sulphuric acid known under the name of " Turkey red oils " have been already described (p. 206, *et seq.*).[1] In the practical manufacture of the castor oil products it is generally considered indispensable to prevent the temperature from rising materially above 35° or at most 40° C.; otherwise secondary reactions take place, leading to evolution of sulphurous acid, and production of inferior products. The oil is run into a wooden tank, preferably lined with sheet lead, and provided with cocks at different heights to facilitate the running off of wash liquors, etc.; the sulphuric acid is then gradually run in with continual agitation, either by hand-worked paddles or by a mechanical agitator.

Considerable differences in the practice of various makers occur in this stage of the process, the precise details of working being usually regarded as trade secrets. In some cases the acid is run in at one operation, more especially when the proportion employed is smaller; in others, part is added at one time, and the rest at intervals; sometimes half being added one day, and the other half the next day. The proportion of acid used also varies considerably,[2] from 15 to 40 per cent. of the weight of oil used.

After standing 14 to 24 hours, a solution of common salt is introduced, and the whole well agitated with the object of removing excess of free sulphuric acid not converted into compound acids, glycerol, glycerosulphuric acid, and such like substances soluble in water, without removing the soluble compound sulphuric acids formed, these being much less soluble in brine than in plain water. If during this washing the liquor become much heated, considerable loss is brought about, because dilute hydrochloric acid is formed which rapidly hydrolyses the compound acids present. Plain water is, therefore, sometimes used for a first washing, and brine or, better still, sodium sulphate solution for subsequent ones.

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[1] A summary of the earlier Bibliography of Turkey red oils is given in the *J. Soc. Chem. Ind.*, 1893, xii., 528. An outline of the later literature is given by Radcliffe and Medofski, *J. Soc. Dyers and Col.*, 1918, xxxiv., 22.

[2] J. A Wilson, *J. Soc. Chem. Ind.*, 1891, x., 26; 1892, xi., 495.

A certain amount of soda or ammonia solution is then run in to the washed oil and well admixed, so as to neutralise part (but usually not all) of the free acidity; and finally enough water is added to bring down the percentage of oleaginous matter present to the required extent, 50 or even less in some cases.

The ultimate product is consequently a sort of emulsion of undecomposed fatty matter and free acids disseminated through an aqueous solution of the soaps formed by the action of the alkali added on the free fatty acids and compound sulphuric acids formed. If properly prepared so as to contain the latter in sufficient quantity, castor Turkey red oil can be diluted with water without allowing oily drops to separate until after standing some considerable time; and may be dissolved in ammonia solution and diluted with water without becoming seriously turbid through separation of oil, etc. If much precipitation is visible solid fatty glycerides are present, due to adulteration of the original castor oil with rape or cotton-seed oil, etc.

According to *P. Lochtin*[1] the risk of spoiling the product prepared from castor oil and sulphuric acid by overheating is much less than is commonly supposed, firstly because no decomposition involving the formation of sulphuric acid is produced at temperatures not exceeding 70° C., excepting that due to albuminoid impurities; and secondly, because in his view only the free fatty acid is of use in the dyeing process, some of the best preparations only containing 2 to 5 per cent. of sulphuric anhydride (SO_3) per 100 of fatty acids (ricinoleosulphuric acid theoretically corresponds with a ratio of 80 parts SO_3 to 298 of ricinoleic acid, or 27 per 100). Moreover, the product of saponification by alkali (necessarily containing no compound sulphuric acid) gives very fine shades in practical dyeing, although the tendency to frothing causes the colour to be a little uneven. The alkali added, he considers, should be ammonia and not soda or potash, because in printing steam colours the alkali is volatilised and the free fatty acid left on the cloth.

In winter 20 to 30 parts, and in summer 15 to 20, of concentrated sulphuric acid are used (in Russia) per 100 of castor oil. About one-half of the acid is stirred gradually into the oil during nine hours of a working day; the mixture is allowed to stand all night, and the next day the rest of the acid is stirred in and the mixture allowed to stand until a sample taken out forms a clear solution, when a few drops are shaken with distilled water in a test-tube; if allowed to stand too long a cloudy fluid is obtained, just as when the action has not been sufficiently prolonged. At the proper time, an equal bulk of cold water is added to the fluid, when the oil separates and floats on the diluted acid solution; if a larger proportion of free fatty acid (hydrolysed sulphuric compounds) is desired, hot water is used instead of cold.

"*Oxyoleates.*"—Formerly this hydrolytic decomposition was usually regarded as the chief thing to be feared and avoided in manufacturing

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[1] *J. Soc. Chem. Ind.*, 1890, ix., 498.

Turkey red oils; but of late years such oils have been placed on the market under the name of "oxyoleates," in the preparation of which the "salted-out" fatty acid is purposely heated to 105° to 120° C., whereby practically all sulphur is eliminated in the form of sulphurous and sulphuric acids (Eng. Pat. 14,430, 1891). According to *Werner*,[1] these products are, for certain applications, superior to the usual Turkey red oils containing sulphonated acids.

Analysis of Turkey Red Oils—*Sulphonated Acids and Unadulterated Glycerides.*—In order to hydrolyse the compound sulphuric acids present, a weighed quantity is agitated with about twice its volume of saturated brine, and about one-tenth its volume of strong hydrochloric acid, whereby hydrolysis is speedily brought about; the product is then shaken up with ether, the ethereal solution evaporated to dryness, and the residue purified by solution in alcohol and filtration to remove saline matters, and evaporation till all alcohol is driven off (*J. A. Wilson*).

The residue is examined so as to determine the amount of unaltered glycerides present with the free acid by the ordinary methods described on pp. 164, 224. The proportion of ricinoleosulphuric acid originally present is ascertained by determining the total amount of barium sulphate obtained from the acid brine, and subtracting from the result the amount present as ordinary sulphate found by agitating the oil with brine and ether in the same way, but without the addition of hydrochloric acid. Obviously the weight of compound sulphuric acid calculated from the corrected weight of barium sulphate thus obtained will be very different according as it is reckoned as ricinoleosulphuric acid or diricinoleosulphuric acid (p. 207), 233 parts of barium sulphate corresponding with 378 parts of the first and with 658 of the second, and consequently with 518 parts of a mixture of the two in equivalent proportions.[2]

Another mode of determining the relative proportions of sulphonated and non-sulphonated acids present is to titrate with standard alkali twice, using litmus as indicator in one case, and phenol-phthalein in the other; the sulphonated acids are given by the first titration, and the others by the difference between the two. *Scheurer Kestner* recommends ammonia as the alkali, notwithstanding the uncertainty of the indications of phenol-phthalein therewith.

Juillard[3] condemns this method of examination as giving inaccurate results, in the light of his own researches (*vide* pp. 49, 208), more especially when diricinolein sulphuric anhydride is present, as is usually the case. He considers that the essential determinations are those of the fatty acids in the usual way, and of sulphuric acid and glycerol after hydrolysis of the oil by boiling with dilute hydrochloric acid.

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[1] *J. Soc. Chem. Ind.*, 1893, xii., 40.

[2] 402 was found by Scheurer Kestner as the equivalent weight of mixed compound sulphuric acids formed in one case, 480 being the corresponding value of the non-sulphonated acids simultaneously produced (ricinoleic acid = 298; diricinoleic acid = 578).

[3] *J. Soc. Chem. Ind.*, 1892, xi., 357; from *Bull. Soc. Chim.*, 1891, vi., 638.

In view of the different shades yielded in dyeing and printing by the various components of the oil, a determination is desirable of the molecular weights of the fatty acids present in the soluble and insoluble states. This may be accomplished by Raoult's method, care being taken to use enough water to bring into solution the whole of the soluble acids. As usually prepared, Turkey red oils contain some 45 or 50 per cent. of oil capable of being separated by means of hydrochloric acid and brine, the balance being water and small quantities of saline matter, etc. Of the separated oil generally about one-fourth consists of unaltered glycerides. The alkali added is usually insufficient to neutralise all the free acid, as a rule only about one-third being neutralised. On addition of water and ammonia to the product a clear emulsion or solution is formed if solid glycerides are absent; but a more or less turbid fluid on account of precipitation if these are present through use of adulterated oil, etc.

The following is a summary of the principal methods most used at present in the analysis of Turkey red oil, more especially of the product obtained by treating castor oil with sulphuric acid :—[1]

Water.—This may be estimated either by *Ubbelohde's* method of distilling a measured quantity of the sample with 30 c.c. of xylene, previously saturated with water, into a narrow cylinder graduated in 0·05 c.c. After distillation of the xylene a further addition is made with a subsequent distillation to expel any residual traces of water, and the volume of the latter is then measured in the cylinder.

Direct Method.—The oil is heated in a platinum basin at 100° C., with constant stirring until successive weighings differ by not more than 0·5 mgrm. In *Richardson* and *Wallon's* experience this gives as good results as the xylene method.

Total Sulphuric Anhydride.—Four grms. of the oil are boiled for 45 minutes with dilute hydrochloric acid, the undissolved fatty matter filtered off, and the sulphate estimated as barium sulphate in the filtrate.

Sulphuric Anhydride as Alkali Sulphate.—A weighed portion of the sample is dissolved in ether, and the solution repeatedly shaken out with sodium chloride solution. The united saline extracts are filtered, and the sulphate precipitated as barium sulphate.

Sodium Chloride.—A weighed quantity of the oil is freed from water, and ignited at a low temperature, and the chlorine estimated volumetrically in a filtered aqueous extract of the ash.

Unsaponifiable Matter.—Ten grms. of the oil are boiled for 60 minutes beneath a reflux condenser with 25 c.c. of 10 per cent. alcoholic potassium hydroxide solution and 100 c.c. of petroleum spirit (b. pt., 40° to 75° C.), and then diluted with 100 c.c. of water. The soap solution is shaken out three times with ether, the united ethereal extracts evaporated, and the residue dried and weighed.[2]

Total Fat.—Ten grms. of the oil are dissolved in 50 c.c. of water, and the solution boiled for 5 minutes with 25 c.c. of dilute (1 : 5) hydrochloric acid, then cooled and shaken with two successive portions of 100 c.c. of ether. The united extracts are washed with water, and evaporated, and the residue weighed. The total fatty oil should be calculated from the difference between 100 per cent. and the sum of the water, ash, and unsaponifiable matter.[3]

Neutral Fat—Herbig's Method.[3]—This is based upon the fact that the

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[1] *J. Soc. Chem. Ind.*, 1912, xxxi., 105.

[2] Method recommended by *Committee of Amer. Leather Chemists' Association* (*J. Soc. Chem. Ind.*, 1914, xxxiii., 32).

[3] *Färber Zeit.*, 1914, xxv., 169, 194.

potassium salts of ricinoleic acid and sulphoricinoleic acid are largely soluble in cold acetone, whereas the sodium salts are so sparingly soluble that the neutral fat may be separated from the sodium salts almost quantitatively by means of acetone.

From 2 to 5 grms. of the oil, according to the amount of water, are neutralised with N/1 or N/10 alkali, evaporated on the water-bath to dryness, and the residue dried with constant stirring in a platinum basin. The dried mass (which must not have been overheated) is boiled with four successive portions (75 c.c. each) of anhydrous acetone, each extract being cooled with ice and decanted through a filter.

The solution is evaporated, the residue of oil weighed, and its acid and saponification values determined. The separated salts are readily soluble in hot water. This solution is treated with boiling hydrochloric acid to liberate combined sulphuric acid and fatty acid, and the latter subsequently extracted with ether and examined.

Sulphonated Oils other than Castor Oil.—At the present time, oils with high iodine values are sulphonated, and in such cases, modified methods of analysis are required.

As a rule, it is necessary to estimate water by the xylene distillation method, since charring may take place on direct heating.

For estimating the *total fat*, *Pickering* [1] recommends the following method :—Five grms. of the sample are dissolved in 50 c.c. of pyridine, hydrochloric acid added, and the flask shaken and allowed to stand for at least an hour on the hot water-bath, with frequent shaking. The liquid is then cooled, shaken in a separating funnel with ether, the ethereal extracts washed until free from acid and pyridine, and evaporated, and the residue dried and weighed.

Hart [2] has devised the following simplified method of analysing sulphonated oils :—

Fat.—A solution of the oil is titrated with N/2 sulphuric acid, using methyl orange as indicator, and the alkalinity (from the soap) is expressed in mgrms. of potassium hydroxide per gramme. Another portion of the sample is taken for the determination of the saponification value in the usual way, and the sum of the two results, divided by the neutralisation value of the fatty acids of the original castor oil, gives the percentage of fat. In cases where the neutralisation value of the fatty acids is not known, the average value of 190 may be taken.

Ammonia.—This is determined by boiling a portion of the solution with a measured excess of N/2 alcoholic sodium hydroxide solution to expel ammonia, and titrating the liquid with N/2 sulphuric acid. The alkalinity of a second portion is then determined, omitting the boiling with caustic soda, and the difference between the two results corresponds with the ammonia.

In calculating the saponification value, allowance must be made for the fat corresponding with the ammonium soap, which acts like fatty acids during the saponification.

Combined Sulphuric Anhydride.—The oil is boiled with a measured quantity of standard sulphuric acid until completely decomposed :—

$$2NaSO_3 . O . C_{17}H_{32}CO_2Na + H_2SO_4 + 2H_2O$$
$$= Na_2SO_4 + 2NaHSO_4 + 2HOC_{17}H_{32} . COOH.$$

It is then titrated with standard alkali solution, using methyl orange as indicator, and the net change in the acidity is equal to the difference between the total alkalinity due to the soap, and the acidity due to the sodium bisulphate.

The total alkalinity of the original sample is determined as described, and from these data the acidity corresponding with the sodium bisulphate, or combined sulphuric anhydride, may be calculated.

Schultz [3] has modified this method in certain details, and shows that, although it yields a higher result for neutral fat than the method of the American Leather Chemists' Association Committee, it may be regarded as trustworthy.

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[1] *Aids in the Commercial Analysis of Oils and Fats*, 1917, p. 65.

[2] *J. Ind. Eng. Chem.*, 1917, ix., 850.

[3] *J. Amer. Leather Chem. Assoc.*, 1918, xiii., 190.

Standard for Sulphonated Oils.—A Committee of the American Leather Chemists' Association has recommended the following as a specification basis for the sale of sulphonated oils:—"The standard shall be 70 per cent. of total fatty oil. Any oil tendered which tests 71 per cent. or over shall be paid for at a *pro rata* increase calculated as from the 70 per cent. standard. Any oil which tests under 70 per cent., but is 68 per cent. or over, shall be subject to a reduction of 1½ times the shortage calculated at *pro rata* price from 70 per cent. If the test falls below 68 per cent. the buyer shall have the right of rejection."

Detection of Cotton-seed Oil Products.—In order to examine Turkey red oil (from castor oil) for adulteration with cotton-seed oil and other glycerides, *Wilson* recommends (*loc. cit. supra*) that a weighed quantity of oil (100 grammes) should be saponified by boiling with methylated spirit (250 c.c.) and pure potassium hydroxide (20 grammes) for an hour under a reflux condenser. After evaporation of the alcohol the residue is dissolved in half a litre of water, and the soap decomposed with a slight excess of sulphuric acid, the whole being boiled for an hour. To avoid bumping, a piece of pumice stone coiled round with platinum wire should be placed in the flask. After standing, the fatty acids are collected by siphoning off the acid liquid through a filter, and washed several times with hot water, and then dried at 100°, and further examined. The specific gravity at 98° C., as taken with a Westphal balance, varies considerably according as the fatty acids are derived from castor, olive, or cotton-seed oil; thus—

Castor oil acids, ...	0·892 at 98° C.
Olive oil acids, ...	0·851 ,,
Cotton-seed oil acids, ...	0·872 ,,

The fatty acids derived from pure castor Turkey red oil, not adulterated with any other oil, do not deposit more than traces of solid matter at 15·5° C., whilst much more is obtained with olive oil, and still larger amounts with cotton-seed oil. The melting points of the latter two acids, when tested by the capillary tube pressure method after solidification, are;—

Cotton-seed oil acids, ...	44° C.
Olive oil acids, ...	40° C.

The neutralisation values of the fatty acids do not differ much—

Castor oil acids, ...	180 to 184
Olive oil acids, ...	173 to 176
Cotton-seed oil acids, ...	171 to 175

The iodine value of the castor oil acids is very variable, being dependent on the age of the castor oil, and the method of preparing the Turkey red oil, especially the amount of sulphuric acid used; so that no indications of any value as regards adulteration can be derived by its means.

The acetyl test, on the other hand, gives indications that are of service in this direction: the fatty acids are boiled for an hour and a half with four-fifths their weight of acetic anhydride under a reflux condenser, and the acetylated product washed with hot water till the washings are neutral to delicate litmus paper. A weighed quantity of the acetylated product is then exactly neutralised with alcoholic potassium hydroxide in the cold (whereby the "acetyl acid value" is obtained, p. 267). Excess of potassium hydroxide is then added (about 1½ times the first amount), and the whole boiled half an hour to saponify acetyl derivatives, the unneutralised potassium hydroxide being finally titrated. The amount of potassium hydroxide neutralised during this second part of the titration (*acetyl value*) varies considerably, according as pure castor oil has been employed, or castor oil admixed with olive or cotton-seed oils; so that whether the observed "acetyl value" is wholly due to the saponification of acetyl derivatives, or (as seems more probable, p. 266) is partly due to the hydration of anhydrides formed by the action of acetic anhydride on fatty acids, in any case it affords a means of detecting adulterations. Thus *Wilson* gives the following averages:—

	Acetyl Acid Value.	Acetyl Value.	Sum (so-called "Acetyl Saponification Value").
Castor oil minimum,	144·0	143·4	287·4
,, maximum,	149·2	138·7	287·9
Olive oil,	158·7	106·3	265·0
Cotton-seed oil,	179·0	53·0	232·0

These acetyl numbers are considerably higher than those yielded by the fatty acids obtained on saponifying olive and cotton-seed oils not treated with sulphuric acid, quoted on p. 268, suggesting that either a considerable amount of hydroxystearic acid, or some analogous substance, is formed by the action of sulphuric acid on olein and saponification of the product; or else that the formation of anhydrides under the influence of acetic anhydride takes place more readily with the fatty acids obtained after treatment with sulphuric acid than with those formed by the saponification of the original oils.

Detection of Hydrocarbons.—Hydrocarbons (petroleum, rosin oils, etc.) are easily detected in Turkey red oil by the process ordinarily used for the purpose described on pp. 169, 177.

CURRIERS' GREASE, SOD OILS, AND DÉGRAS.

During certain operations for tanning and currying skins, various forms of oil and grease are worked into the skin mechanically, and the excess subsequently removed, partly by pressure, partly by the emulsifying and saponifying action of alkaline solutions. When these fluids are decomposed by an inorganic acid an oily mass results, partly consisting of free fatty acids and partly of undecomposed glycerides.

When tallow has formed part of the original grease or "dubbin" employed, the resulting recovered grease is of thicker consistency than that obtained when only liquid oils have been employed, such as olive oil, whale or cod oil, or menhaden oil. The greases thus obtained, or regained by pressure only, are sometimes known as "sod oils" or "dégras." When cod oil and similar substances are absorbed in skins and exposed to the air, a certain amount of oxidation is brought about, rendering the regained oil even better for use than the original unoxidised material; accordingly it is sometimes the practice (more especially in France) to prepare sod oil (*Möellon*) for currying by absorption in skins used solely for the purpose, and subsequently wrung out again after sufficient exposure to the air.

Part of the good effect produced by sod oil and grease that has been already used previously is supposed by some to be due to the presence of tanning matters dissolved out from the leather and contained in a condition peculiarly adapted to the finishing of the tanning process in another skin; others believe that the beneficial effect is at least partly due to the solution in the grease of nitrogenous matters not affected by tanning and their subsequent removal by squeezing out the greasy solution, especially if the operation is done hot. The recovered dégras at any rate contains more or less nitrogenous matter, which is left undissolved as a resinoid mass when the material is treated with light petroleum spirit; further, a considerable amount of hydroxyoleic acid (or some similar hydroxy acid, such as dihydroxypalmitic acid) is usually present, and in the case of dégras made from train oils, more or less cetylic alcohol and similar bodies produced by the hydrolysis or saponification of their compound esters, together with cholesterol. The presence of these substances enables fatty matters to become emulsified with water and thus to penetrate the tissues more readily, just as in the case of lanolin applied to a living skin (*infra*).[1]

Artificial dégras, curriers' greases and dubbin are prepared by intermixing tallow and cod oil or similar materials, red oil (crude oleic acid from the candle factory, Chap. XVII.) and wool-grease sometimes entering into the composition, together with neutral soap or imperfectly made soap prepared by heating together oil with an amount of alkali insufficient to saponify it completely. These products, however, are generally regarded as greatly inferior to that prepared by the oxidation of cod or other fish oils in contact with skins, so that, for the finer kinds of French leather, only the latter are employed.

Sod oils obtained by simple pressure from skins treated with olive, cod, or menhaden oil are valuable when properly refined for the lubrication of delicate machinery (clocks and watches, etc.), not being liable to clog and thicken.

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[1] For analyses of various kinds of dégras, and a discussion of their general nature, *vide J. Soc. Chem. Ind.*, 1891, x., 557; 1892, xi., 639.

Hopkins, *Coburn*, and *Spiller* [1] draw a distinction between dégras and sod oil, defining the former as oil extracted from the skins in the manufacture of chamois leather, and the latter as the waste oil from ordinary leather after currying.

Sod oil is light yellow to dark brown in colour, and contains "dégras former," a resinous substance (m.p. 65° to 67° C.) which can be extracted from the oil with petroleum spirit, although in a pure state it does not dissolve in that solvent.

It can be determined by saponifying the oil, precipitating the soap with salt, filtering, precipitating the "dégras former" from the filtrate by means of hydrochloric acid, washing it with water and petroleum spirit, and dissolving it off the filter into a weighed dish with absolute alcohol, which is subsequently evaporated.

The following analyses, made by *Hopkins*, *Coburn*, and *Spiller*, show the composition of twelve representative samples :—

	Per cent.
Total ash,	0·05- 1·045
Moisture,	1·01-40·61
Oil, &c., soluble in petroleum spirit,	56·62-96·60
Soap, &c., soluble in alcohol,	0·68- 8·81
Hide fragments,	0·15- 2·99
Ash, insoluble in petroleum spirit and alcohol,	0·06- 0·47
"Dégras former," calculated on anhydrous oil,	1·09-26·44
Unsaponifiable matter,	0·37-24·62
	Milligrammes.
Total KOH consumed by 1 gramme anhydrous oil,	105·64-204·13
Mineral acid, in terms of KOH,	1·13- 91·51
Total ,, ,, ,,	33·78-125·77
Variation in Reichert-Meissl value,	1·74- 5·07
Iodine value,	38·37-78·32

MANUFACTURE OF LANOLINE.

Wool, as cut from the sheep's back, is largely impregnated with a greasy material, *suint*, the evaporated perspiration of the animal ; this partly consists of various natural potassium salts and soaps soluble in water, partly of cholesterol and isocholesterol and their stearic and other compound esters, and to a small extent of cerylic cerotate, and other waxy organic matters.

When solvent processes are employed for dissolving out the grease (*e.g.*, by means of ether or carbon bisulphide), the substance obtained by distilling off the solvent is a tarry brown mass of unpleasant odour, of specific gravity at 15° C. about 0·973, melting at about 40° C., sparingly soluble in alcohol, and only saponifiable with difficulty, as the cholesterol esters are comparatively very stable. The "wool-grease" thus obtained is usually distilled by means of superheated steam,

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[1] *J. Amer. Chem. Soc.*, 1899, xxi., 291.

whereby a mixture is produced mainly consisting of free fatty acids and cholesterol, from which "wool-stearine" is obtained by expression. Methods for cleansing wool by means of grease solvents have not come largely into use in Britain, it being usually considered that the heating required to remove the residual solvent from the wool does more injury than the action of soap in the ordinary wet process of wool scouring. Opinions on this point, however, are by no means unanimous.

On the Continent, wool cleansing by means of solvents has made much more progress, and a variety of different forms of apparatus have been patented, in which the use of ether, fusel oil, carbon bisulphide, light petroleum spirit, benzene, etc., has been claimed.[1]

By treatment with water, fleeces yield a solution of potassium soaps in which the cholesterol and other compound esters, etc., are emulsified. The extraction from the aqueous product thus formed of a purified emulsion for medicinal purposes was described by Dioscorides in the first century A.D., under the name of 'Οίσυπος; a more refined preparation of the kind has of late years been somewhat largely employed under the name of *lanoline*.

Lanoline.—To prepare this material, *Braun* and *Liebreich* (Eng. Pat. 4,992, 1882) subject the suds in which fleeces have been washed (or a mixture of wool-fat and soap-water forming an analogous emulsion) to centrifugal action, whereby a separation is effected somewhat analogous to that produced in a cream separator; watery soap solution flows away, whilst a soft grease along with solid dirty particles is retained. The former is subjected to treatment with acids, etc., for the recovery of the fatty acids contained in the soap (Chap. XII.); the latter is purified by kneading with water, melting, and filtration, or solution in appropriate solvents, followed by further kneading with water until all soluble impurities are washed away.

The purified greasy matter thus obtained possesses a remarkable power of forming a soft lard-like mass by the intimate mixture of water and grease so as to form a stiff semi-solid emulsion. On account of the peculiar utility of this product as a vehicle for enabling drugs, etc., to be passed into the body by rubbing on the skin, lanoline, impregnated with the desired active material, and its use as an emollient unguent, either alone or in combination with other materials, has of late years come somewhat prominently before the public; as also have various other substances differing from it in no essential particulars except the trade name, and in possessing varying degrees of purity.

Several modifications of Braun and Liebreich's centrifugal separation process have been subsequently introduced. In one of these, calcium chloride, or other similar salt, is added to the water so as to form insoluble lime salts or other metallic soaps. The separation of the grease is thus facilitated, whilst by means of hot acetone the

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[1] For a description of Singer and Judell's arrangements, in which carbon bisulphide is used as solvent, *vide* a paper by Watson Smith, *J. Soc. Chem. Ind.*, 1889, viii., 24.

cholesterol esters, waxes, etc., present are subsequently dissolved out from the soaps. After distillation of the solvent, the residual purified wool-grease is treated with oxidising agents to remove animal odour and lighten the colour, and is then kneaded with water till the requisite consistency is attained.

Other processes of a fractional solvent character are also employed to separate from the crude "anhydrous lanoline"[1] some of the waxy ingredients, and thus obtain a product consisting principally of cholesterol, isocholesterol, and their esters, and, in consequence, better adapted to form a semi-solid emulsion with water, suitable as an unguent, etc.

Some of the products sent into the market and sold as "purified wool-grease," or under various fancy names (*e.g.*, *agnin*, *anaspalin*, *alapurin*, etc.),[2] are of much less desirable character than others. *Levinstein* gives the following tests as those by which the purity of commercial lanoline may be ascertained :—

1. If 2 to 3 grammes of lanoline be heated with 10 c.c. of a 30 per cent. sodium hydroxide solution, no ammonia must be liberated.

2. Ten parts lanoline heated with 50 of distilled water must yield a clear oil. Impure lanoline becomes frothy and turbid.

3. If oily, the lanoline thus separated must be free from glycerol.

4. If rubbed with water with an iron spatula on a ground glass plate, the oil must be capable of taking up at least its own weight of water, forming a sticky and paste-like mass; if impure, the mass will have a soap-like smoothness, and will not adhere to the spatula.

Langbeck[3] describes the following process for preparing a purified lanoline :—The wool is washed twice in water at a temperature not exceeding 110° F., and dried by pressure or centrifugal action, whereby soluble potassium salts are, for the most part, removed. The residual wool is then scoured with a mixture of potash lye and olive oil, whereby all the "wool-fat" is removed and the wool thoroughly cleansed. The aqueous emulsion is evaporated and treated with alcohol of 40 to 60 per cent., which dissolves out potassium soaps, leaving behind crude "wool-fat," purified by solution in benzene or carbon bisulphide, filtration, and distillation of the solvent. The product, after further purification and decolorisation with animal charcoal (preferably "prussiate waste"), and subsequently with peroxide of hydrogen, produces an excellent white basis for pomades, ointments, etc., containing 20 to 30 per cent. of mechanically intermixed water. The unpurified wool-fat forms a valuable lubricant and leather-grease.

A. Seibel has introduced a sulphonated lanoline (German Pat. 56,491) for medicinal and other purposes, prepared by heating lanoline to 120° C. with about 20 per cent. of flowers of sulphur, whereby

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[1] *Vide* Levinstein, *J. Soc. Chem. Ind.*, 1886, v., 579.

[2] According to a statement in the *Chem. Zeit.*, 1900, 306, the German patents for lanoline having expired, and the use of the term "lanolin" is no longer permitted by the German Patent Office.

[3] *J. Soc. Chem. Ind.*, 1890, ix., 356.

most of the sulphur is dissolved. After standing for some time, the supernatant sulphur-containing liquid is poured off and heated to 230° C., whereby much sulphuretted hydrogen is formed, together with the sulphonated lanoline. Like ordinary lanoline, this mixes freely with water without separation, forming a soft semi-solid emulsion.

In order to obtain colourless wool-fat, the *Norddeutsche Wollkämerie* (German Pat. 55,056, 1890) use sulphurous acid instead of hydrochloric or sulphuric acids for the separation of the fatty mass from the wool scourings.

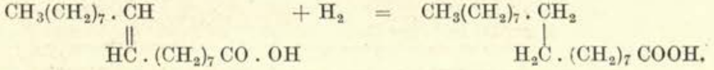
CHAPTER XV.

HYDROGENATED OILS.

Some description has already been given of the various attempts which have been made to convert oils into solid fats, such as, for example, the process of fusing oleic acid with potassium hydroxide (p. 27), or of treating liquid fatty acids with sulphuric acid (p. 205) or zinc chloride (p. 203). At best, these methods were only partially successful, since only a part of the liquid fatty acid was converted into solid material, whilst the products were only suitable for technical purposes, such as the manufacture of candles, and could not be used as constituents of food.

Although unsaturated fatty acids and their glycerides will readily combine with chlorine or bromine to form saturated compounds, all attempts to bring about a similar absorption of hydrogen were, until a few years ago, unsuccessful. It was not until *Sabatier* and *Senderens*[1] published their investigations that a solution to this difficult problem was found. In these investigations it was shown that on treating certain unsaturated compounds in vaporised condition with hydrogen in the presence of a catalytic agent, such as finely divided platinum or palladium, combination of the gas with the unsaturated substance was readily effected, while the metallic catalyst was apparently unaffected.

In the case of oleic acid, for instance, the reaction is as follows :—



$$\begin{array}{llll} CH_3(CH_2)_7\,.\,CH & +\ H_2 & = & CH_3(CH_2)_7\,.\,CH_2 \\ \quad\;\, \| & & & \quad\;\, | \\ \quad HC\,.\,(CH_2)_7\,CO\,.\,OH & & & \quad H_2C\,.\,(CH_2)_7\,COOH. \end{array}$$

The principle thus established was soon applied to oils and fats, and when once it had been found practicable it became the basis of commercial processes, and the subject of numerous patents.

Processes of Hydrogenation.—The earliest process of hydrogenating oils appears to be that of *Le Prince* and *Liveke*, which was patented in 1902 in Germany. In the following year a process upon similar lines was protected by *Normann* (Eng. Pat. 1,515, 1903). The vaporised fatty acids were passed, together with hydrogen, through a layer of porous pumice stone upon which had previously been deposited a coating of finely powdered nickel or other catalytic agent. *Normann* also claimed the process of hydrogenating the oils themselves.

His patent is of interest in view of the fact that it was regarded as a master-patent, precluding all other processes of hydrogenating oil. As the result of a legal action, however, it was held in 1913 that

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[1] *Comptes Rendus*, 1900, cxxx., 723 ; cxxxi., 187.

the patent was not valid, since the details disclosed therein were insufficient to insure successful hydrogenation.

The process devised by *Bedford* (Eng. Pat. 9,112, 1908) is concerned only with liquid fatty acids, which are sprayed on to beds of catalytic material, where they meet a current of hydrogen heated to about 200° C. under reduced pressure. In a German patent of *Erdmann* (1907) a similar process is applied to the oils, which are sprayed on to a porous catalytic material heated to 170° to 180° C., where they meet a current of hydrogen.

The use of metallic palladium as the catalyst is claimed in another patent (Eng. Pat. 18,642, 1911), where it is stated that it is a much more effective agent than nickel, being capable of bringing about the hydrogenation of 100,000 times its weight of an oil.

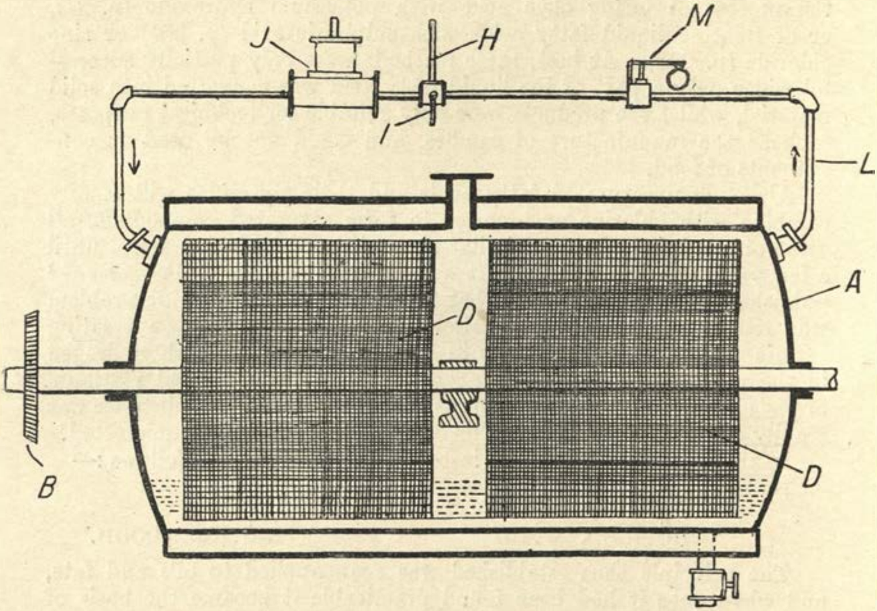

Fig. 100.—Kayser's Hydrogenating Apparatus.

A. Closed horizontal cylindrical vessel.
B. Driving gear.
D. Paddle-wheel.
H. Hydrogen admitted.
I. Three-way cock.
J. Compression pump.
L. Exhaust pipe.
M. Blow-off valve.

The modifications of the forms of apparatus whereby the oil, the hydrogen, and the catalyst can be brought into intimate association are very numerous, and have been made the subject matter of several well-known patents.

For example, in *Kayser's* process (U.S. Pat. 1,004,035, 1911) the apparatus consists of a closed cylinder in which revolves a paddle-wheel, the blades of which are covered with wire gauze. The mixture of oil and catalyst is introduced into this cage, while a current of hydrogen is passed through the cylinder, the temperature of which is maintained at about 150° to 160° C (see Fig. 100).

In order to effect more rapid hydrogenation at a relatively low temperature, and thus prevent alteration of the properties of the oil, *Wilbuschewitz* (1912) has devised an apparatus in which the oil is introduced as a fine spray into a series of connected autoclaves or pressure tanks, where it meets a current of hydrogen under a pressure of about nine atmospheres, and is rapidly hydrogenated at temperatures between 100° and 160° C.

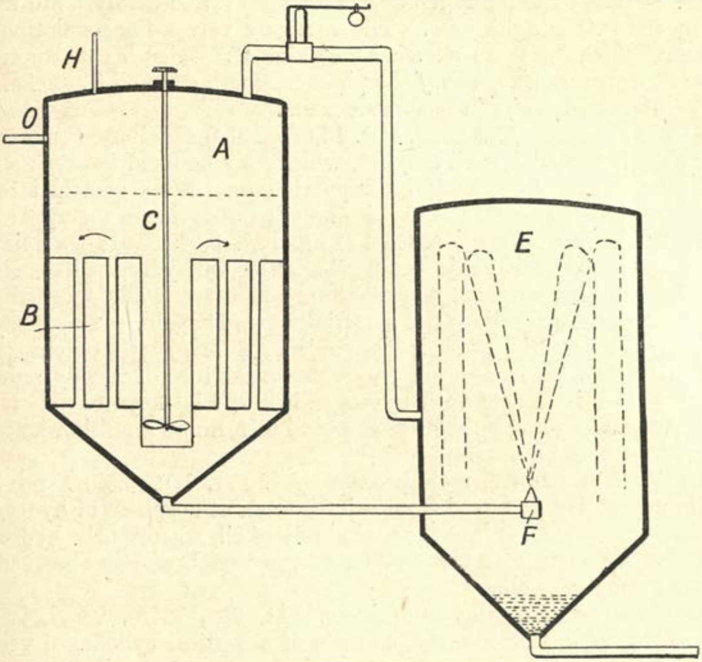

Fig. 101.—Testrup's Apparatus for Hydrogenating Oil.

O. Pipe for pumping in oil and catalyst.
A. Tank.
B. Tubes.
C. Stirrer.
E. Tank.
F. Spray nozzle.

Another modification, due to *Schlink & Co.* (Eng. Pat. 8,147, 1911), consists of a series of drums containing porous catalytic material, through which the oil and hydrogen are driven by means of centrifugal force. In an apparatus patented by *Ellis* (U.S. Pat. 1,026,156, 1912) porous catalytic material is introduced into tubes, which can be heated to the required temperature at any point. The oil is pumped through these tubes, and encounters a current of hydrogen coming from the opposite direction.

A diagram of *Testrup's* apparatus is shown in Fig. 101. The mixture of oil and finely divided catalyst is sprayed into a closed chamber, through which hydrogen is passed, and is then withdrawn from the chamber to be returned to the spraying device, or is transferred to other chambers for further treatment (Eng. Pat. 7,726, 1910). For example, the oil may be heated to the necessary temperature in vessel A and hydrogen introduced at a pressure of 15 atmospheres. Thence it is sprayed into B, where the hydrogen is admitted at, say, 12 atmospheres, so that the pressure is lower than in A. In like manner hydrogen at successively lower pressures is introduced into the succeeding vessels, so that the oil is thrown as a spray into each in turn. The oil is introduced at *b* and the hydrogen at *c*, and the oil and catalyst are mixed by means of the agitator *a*. The reducing valves for regulating the pressure of the gas are shown at *d′* and *d″*, whilst *e e e e* represent pipes for superheated steam, *f* the pipes conducting the oil from chamber to chamber, and *g*, *g′*, *g″* the spray nozzles.

Dewar and *Liebmann* (Eng. Pat. 15,668, 1914) distribute the catalyst over fibrous material, such as yarn, which may be fixed between sheets of wire gauze. These may be supported on frames attached to an agitator or wound round the blades of a stirring device in the apparatus.

According to *Calvert's* process (Eng. Pat. 5,969, 1914), a mixture of oil and catalyst is subjected to the action of hydrogen in a closed vessel containing a rotating comb-shaped agitator, while a centrifugal propeller at the base flings the material upwards again.

Effective emulsification is the object of *M'Elroy's* patent (U.S. Pat. 1,157,993, 1915), according to which a mixture of freshly reduced nickel and oil is treated with hydrogen in a special form of apparatus, so that the ascending bubbles of gas tend to form an emulsion between the hydrogen and the oil.

In *Birkeland* and *Devik's* process (U.S. Pat. 1,125,259) a mixture of oil and catalyst is forced from a jet into an atmosphere of hydrogen, and thence downwards into the main body of oil, whereby the hydrogen is carried by suction to the bottom of the vessel, and is absorbed as it rises through the oil.

Lane's apparatus (Fig. 102) (Eng. Pat. 968, 1915), which is extensively used in this country, consists of a vertical cylindrical vessel, which is heated by means of a steam jacket or other suitable device. Beaters, rotating horizontally round a central shaft, alternate with annular sloping shelves on the sides of the vessel, so that the oil introduced at the top is alternately sprayed outwards to the sides, and guided to the centre of the beaters next below, and so on, until it reaches the bottom, and is then pumped to the top again. Further details of the use of this apparatus are given below.

Richardson (U.S. Pat. 1,177,896, 1916) makes use of an electric arc produced between nickel electrodes, which are immersed in the oil, so that part of the metal is disintegrated and becomes incorporated with the oil. Hydrogen is then passed through the vessel, and, after hydrogenation, the disintegrated metal is separated from the oil.

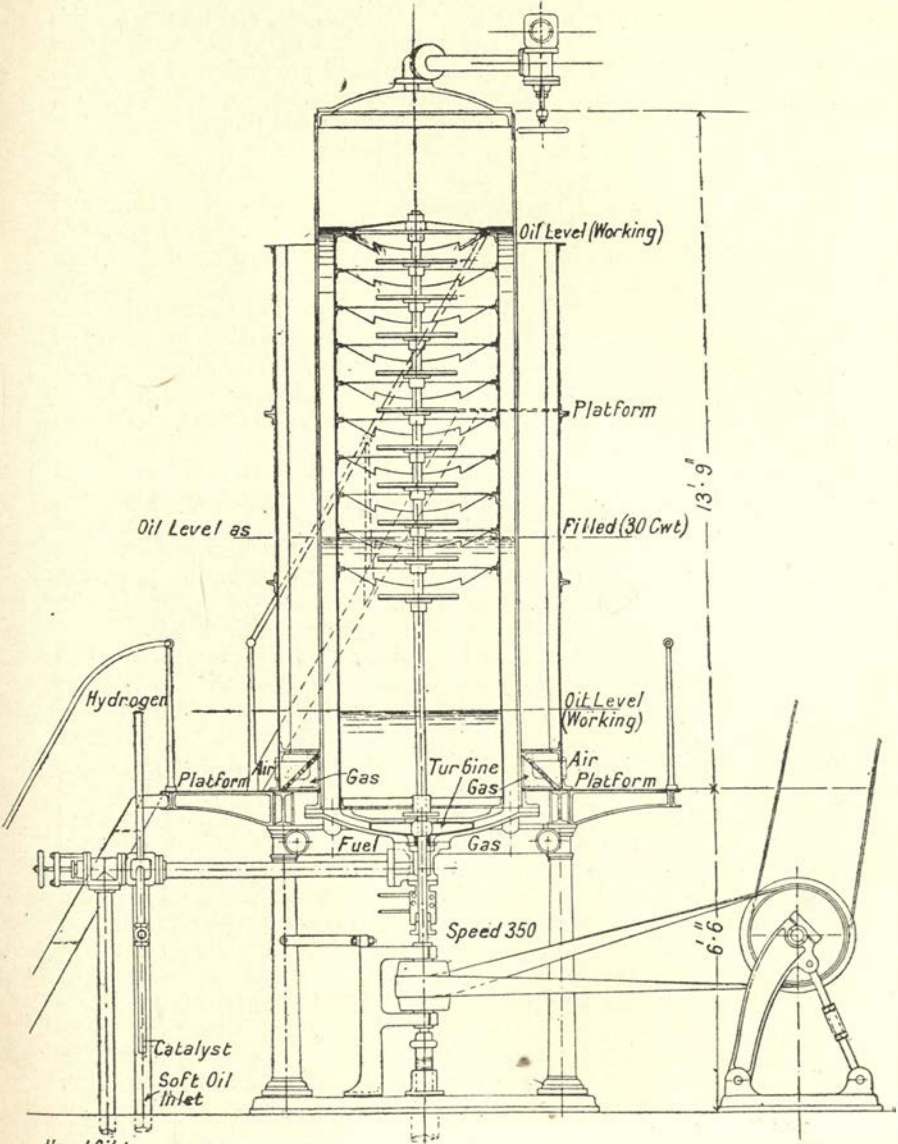

Fig. 102.—Lane's Hydrogenising Plant.

Sectional Elevation of Autoclave.

The Catalytic Agent.—In the experiments of *Sabatier* and *Senderens* (*supra*), palladium was used as the catalytic agent, and its use for this purpose was continued in the early processes of hydrogenating fats. It has the advantages that only a very small proportion of the metal is required to effect the hydrogenation of very large quantities of oil, at a relatively low temperature, and in a very short time (*Paal*).[1]

On the other hand, the high cost of palladium in comparison with nickel has prevented its general adoption in industrial processes. In addition to nickel and its compounds, the use of copper, iron, and other metals is claimed in various patent processes. *Paal* (*loc. cit.*) found that platinum black was much less effective as a catalyst than colloidal palladium.

The method of preparing the nickel catalyst is of essential importance in the process. The hydroxide is first precipitated by means of alkali from a solution of nickel sulphate (*Crossfield*, Eng. Pat. 30,282, 1910), or preferably nickel nitrate, to obviate the presence of traces of sulphur compounds, and is then washed, dried, and reduced by means of a current of hydrogen.

In order to obtain the reduced metal in the finest possible state of division, it is necessary to reduce it at as low a temperature as possible. Reduction is incomplete at 250° C., and in practice it has been found that a temperature a little above 300° C. gives the best results. The activity of the catalytic agent is increased by distributing it over a porous medium, such as pumice stone, kieselguhr, or charcoal, with the object of bringing it into more intimate contact with the oil.

When once prepared it must be protected from atmospheric oxidation, and must not be allowed to come in contact with substances which destroy its activity, such as, for example, traces of arsenic or phosphorus in the hydrogen (*vide infra*). To obviate the difficulty of preventing oxidation of the nickel, and to obtain a catalyst which is less sensitive to traces of chlorine or sulphur, which may be liberated from proteins in the oil, *Bedford* and *Erdmann*[2] make use of oxides of nickel. In the case of the higher oxides, they claim that the final product of the reduction within the oil is not metallic nickel, but a nickel sub-oxide. For hydrogenation on a small scale, the oil is placed in a cylinder of quartz glass or copper, which is fitted with a mechanical agitator, and this is heated in an oil-bath at 180° C. while a current of hydrogen is introduced. Small quantities of nickel oxide are then added, the temperature raised to 255° to 260° C., more catalyst introduced, and the supply of hydrogen increased. The oil thus hydrogenated is free from hydroxy acids, whilst nickel soaps are only formed to a limited extent. The process has been patented (Eng. Pat. 27,718, 1912).

Meigen[3] considers that, while it is conceivable that a suboxide or hydride of nickel may be the actual catalyst under these conditions, there is no evidence in support of the hypothesis.

Numerous other patents deal with the nature and preparation of

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[1] *Ber.*, 1908, **xli.**, 2282.

[2] *J. prakt. Chem.*, 1913, lxxxvii., 425.

[3] *J. prakt. Chem.*, 1914, lxxxix., 290.

the catalyst. *Higgins* (Eng. Pat. 18,282, 1912) adds from 1 to 2 per cent. of an organic acid such as formic acid to accelerate the hydrogenation.

A novel process is claimed by Lessing in Eng. Pat. 18,998, 1912, according to which hydrogen containing 5 to 10 per cent. of carbon monoxide, as would be obtained from water-gas, is passed over reduced nickel, whereby nickel carbonyl is formed. The mixture of this with hydrogen is conducted into the oil, which is heated to about 200° to 240° C., with the result that the nickel carbonyl is decomposed, leaving metallic nickel in a very active condition.

In *Byrom's* process (Eng. Pat. 13,382, 1913) the catalyst is prepared by treating the solution of a nickel salt, such as the nitrate, with an alkali silicate, and drying and reducing the precipitate. It is claimed that a catalyst thus prepared retains its activity longer than the usual catalysts.

Richardson (U.S. Pat. 1,157,718, 1915) claims the use of an oleate of nickel or other metal dissolved in the oil and reduced by hydrogen, whilst *Ellis* (U.S. Pat. 1,156,068, 1915) incorporated a finely divided hydrated nickel hydroxide, $Ni(OH)_2 . H_2O$, with the oil, reduced the mass with hydrogen, and removed the water.

According to a patent of the *Bremen-Besigheimer Oelfabriken* (Eng. Pat. 4,023, 1915), organic compounds of metals, such as nickel benzoate, are calcined with carbon, and the resulting mass kept in oil until required for use. It is claimed that by means of this catalyst oils can be hardened at 150° to 200° C., whilst the carbon has a deodorising and decolorising action.

As the impurities contained in certain fish and whale oils have a toxic action on the catalyst, various methods have been proposed to remove these substances. *Ellis* (U.S. Pat. 1,078,136, 1913) dilutes these oils with a neutral oil prior to hydrogenation. Another method, described by *Ellis* and *Wells*,[1] is to agitate the oil and heat it with freshly precipitated copper hydroxide, which removes the injurious substances, especially if the oil has first been treated with sodium carbonate solution. In other cases filtration of the oil and addition of a fresh quantity of catalyst, are necessary.

The action of various substances in promoting or checking the catalystic hydrogenation of oils has been studied by *Ueno*,[2] who classifies the various compounds, according to their behaviour. Powdered metals (not reduced by hydrogen), such as nickel, tin, zirconium, and copper, have no pronounced injurious effect, but iron, zinc, lead, and mercury act as poisons.

Preparation of the Hydrogen.—It is essential that the hydrogen used for the catalytic hydrogenation of oils should be of a high degree of purity, and in particular that it should be practically free from chlorine, sulphur, phosphorus, and arsenic, and contain not more than traces of oxygen and carbon oxides. Electrolytic decomposition of

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[1] *J. Ind. Eng. Chem.*, 1916, viii., 886.

[2] *J. Chem. Ind., Tokyo*, 1918, xxi., 898.

water containing a small amount of sulphuric acid or an alkali yields a very pure hydrogen, containing as impurity only about 0·2 per cent. of oxygen.

In the *Linde-Frank-Caro* method the liquefied components of water-gas are distilled, and the hydrogen is then purified (up to about 99·5 per cent.) by being passed over soda-lime heated to 180° C.

In *Lane's* process hydrogen is produced by passing steam over red-hot iron—

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2,$$

and the iron oxide is then reduced to iron again by means of a gas, such as producer gas, containing carbon monoxide—

$$Fe_3O_4 + 4CO = 3Fe + 4CO_2.$$

The two processes are carried out successively so long as a sufficient velocity of reaction is maintained (Eng. Pats. 10,536, 1903; 17,591, 1909; 11,878, 1910).

The *Soc. Lyonaise du Gaz* uses roasted pyrites, and the *Greisheim Elektron Company* decomposes water-gas by means of a mixture of lime and iron. Another method, which is employed in countries with a supply of petroleum, is the *Rincker-Wolter* process, in which the hydrocarbons of oil-gas are decomposed at a high temperature into carbon and hydrogen.

Details of the cost of hydrogen plant and the working expenses are given by *Bontoux*.[1]

Technology of Hydrogenation.—The writer is indebted to Mr. H. Lane for the following details of the working of his process:—The crude oil is dried first in heating vessels provided with agitators, and subsequently in vacuum pans containing a steam coil and an agitator.

The catalyst is prepared by mixing together a solution of nickel sulphate and sodium carbonate in a mixing tank, which contains an absorbent material such as kieselguhr. The sludge, consisting of the inert material and the precipitated nickel carbonate, is dried in a hot-air stove, ground up, and roasted to convert the carbonate into oxide, and is then reduced in a current of hydrogen. One form of apparatus used for this purpose is a vertical vessel provided with means of heating. The powdered material is introduced into the top, whilst the current of hydrogen is admitted at the base. The powder falls on to a series of reciprocating grids, the movement of which exposes fresh portions of the heated material to the action of the gas, and finally the reduced substance falls into a tank containing oil of the same kind as is to be hydrogenated. After thorough admixture, the black oily mass is ground to a suitable consistence.

To avoid discolouring the oil during the hydrogenation, the combination is effected at a temperature of about 180° to 200° C., under a pressure of 70 to 80 lbs. to the square inch.

The autoclave (see diagram, p. 449) is a cylindrical vessel surrounded by a jacket of fire-brick forming the flue from a separate furnace.

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[1] *Les Matières Grasses*, 1914, vii., 4194.

The agitating device consists of a series of square heating discs mounted on a vertical shaft, and a number of cones having square holes in their centres and attached to the walls of the vessel. The mixture of oil and catalyst and the hydrogen are introduced as shown, whilst the vessel is connected with a vacuum pump. The oil is drawn

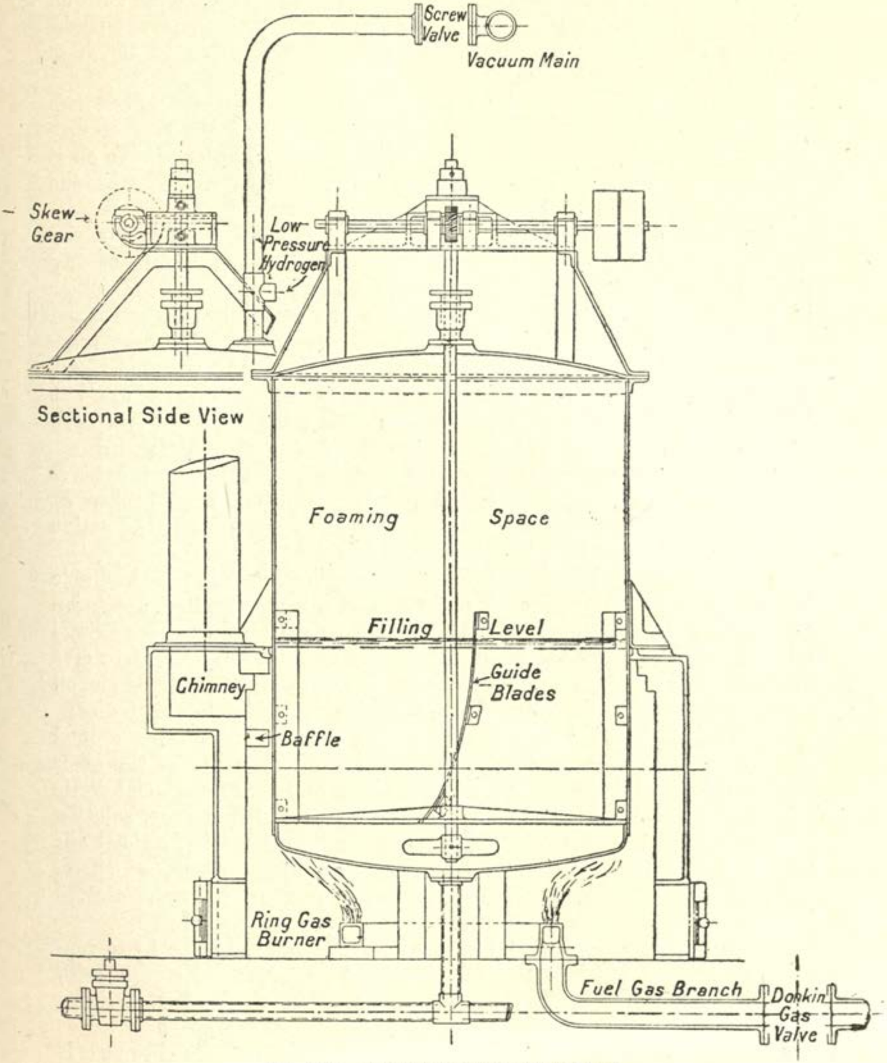

Fig. 103.—Lane's Hydrogenising Plant.
Sectional Elevation of Pan.

from the bottom of the vessel by means of a pump, and continually thrown to the top again on to the uppermost cone. Thence it is driven against the sides of the vessel, thrown back and discharged through the opening on to the second cone, and so on, until it reaches the bottom. To prevent the hot walls of the vessel affecting the oil, recent modifications of the apparatus have the agitator extending to the base and provided with a heater.

On pumping hydrogen into the autoclave the pressure first rises and then becomes stationary at a point depending on the temperature of the oil. As soon as samples appear sufficiently hardened, the oil is drawn off, cooled slightly, and filtered through a press. The residue in the press is broken up and made ready for a fresh charge.

Hardened or Hydrogenated Fats.—By varying the duration of the hydrogenating process it is possible to convert oils into fats of any desired degree of hardness, from a soft fat like butter to a hard tallow of high melting point. The longer the hydrogenation is continued the lower becomes the iodine value, until eventually it become practically *nil.* The refractometer value is also reduced, but the acid value, saponification value, and amount of unsaponifiable matter are but little affected. In the case of oils containing hydroxyl groups, such as castor oil, the hydroxyl value is lowered (*Normann* and *Hugel*).[1]

Characteristic colour reactions of certain oils, such as the silver nitrate test and Halphen's test for cotton-seed oil, are checked or inhibited by hydrogenation, but the sesamol of sesamé oil, the active agent in Baudouin's test, is not affected (*Kreiss* and *Roth*).[2]

Hydrogenation interferes with the application of the insoluble bromide test for marine animal and fish oils, a much smaller proportion of bromides being obtained after the treatment. Certain marine animal oils, however, such as whale oil, have been found by *Grimme* [3] to give distinctive colorations after hydrogenation. For example, whale oil gives a violet coloration when treated with sulphuric acid and iodine.

Tortelli and *Jaffe* [4] describe a specific reaction of marine animal oils, which is not destroyed by hydrogenation. One c.c. of the oil is dissolved in a mixture of 6 c.c. of chloroform and 1 c.c. of glacial acetic acid, and the solution shaken with 40 drops of a 10 per cent. solution of bromine in chloroform. Under these conditions marine animal oils give a pink coloration, changing rapidly to a bright green, which remains for over an hour. Other oils give, at most, a yellow coloration in this test.

According to *Leimdörfer*,[5] the stearic acid formed in the hydrogenation of fatty acids is chemically identical with natural stearic acid, but there are differences in chemical and physical characteristics between the stearin of hydrogenated and of natural fats.

Arachidic acid may still be detected in hardened arachis oil, but it is necessary to fractionate the fat before applying the test. For this

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[1] *Chem. Zeit.*, 1913, xxxvii., 815.

[2] *Zeit. Nahr. Genussm.*, 1913, xxv., 81.

[3] *Chem. Rev. Fett Ind.*, 1913, xx., 155.

[4] *Annali Chim. Applic.*, 1914, ii., 80.

[5] *Chem. Zentralbl.*, 1914, i., 304.

purpose *Kreis* and *Roth*[1] separate the insoluble fatty acids by the lead-ether method, and crystallise them from ether. If the deposit melts above 70° C. arachis oil was probably present.

Phytosterol and cholesterol are not affected to any appreciable extent by hydrogenation at low temperatures, so that in some cases the presence of an animal fat may still be detected by the cholesteryl acetate test. Cholesterol is more affected than phytosterol in the process. Thus, it has been shown by *Marcusson* and *Meyerheim*[2] that 75 per cent. of the cholesterol in an oil becomes resinified by hydrogenation at 200° C., whilst phytosterol is not appreciably attacked. After hydrogenation at 250° C. cholesterol no longer forms crystalline derivatives.

Analytical Values of Hydrogenated Fats.—*Bömer* and *Leschly-Hansen*[3] obtained the following results with oils hydrogenated in an autoclave in the presence of nickel reduced on kieselguhr :—

Oil.	Melting Point.	Solidification Point.	Refractometer Reading at 40° C.	Acid Value.	Saponification Value.	Iodine Value.	Iodine Value of Liquid Fatty Acids.
	°C.	°C.					
Arachis, . .	51·2	36·5	50·1	1·0	188·7	47·4	82·9
Sesamé, . .	47·8	33·4	51·5	0·5	190·6	54·8	88·9
Sesamé technical, .	62·1	45·3	38·4 (at50°C.)	4·7	188·9	25·4	. .
Cotton-seed, .	38·5	25·4	53·8	0·6	195·7	69·7	115·6
Whale, . .	45·1	33·9	49·1	1·2	192·3	45·2	96·0
Coconut, natural, .	25·6	20·4	37·4	0·3	255·6	11·8	. .
Coconut, hydrogenated, .	44·5	27·7	35·9	0·4	254·1	1·0	. .

The following values of a typical hard and soft fat obtained by hydrogenating a marine animal oil are given by *Grimme*[4] :—

Specific Gravity at 15° C.	Melting Point.	Solidification Point.	Refractive Index (40° C).	Acid Value.	Saponification Value.	Iodine Value.
	° C.	° C.				
0·9271	47·2	34·9	1·4529	1·94	189·3	23·24
0·9200	38·5	31·6	1·4575	1·00	188·8	58·34

The following examples, given by *Ellis*,[5] show the effect of hydrogenation in lowering the refractive index :—Maize oil, 1·4514 ; whale, 1·4550 ; soya bean, 1·4538 ; coconut " olein," 1·4425 ; linseed, 1·4610 ; palm, 1·4517 ; and arachis oil, 1·4547.

[1] *Zeit. Nahr. Genussm.*, 1913, xxv., 81.
[2] *Zeit. angew. Chem.*, 1914, xxvii., 201.
[3] *Chem. Rev. Fett Ind.*, 1912, xix., 218, 247.
[4] *Ibid.*, 1913, xx., 129.
[5] *J. Ind. Eng. Chem.*, 1914, vi., 117.

Hydrogenated fats, prepared from whale oil in Germany for manufacture into margarine, were found by *Sandelin* [1] to have the following characteristics :—

	Melting Point.	Solidification Point.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Molecular Equiv. of Fatty Acids.	Melting Point of Arachidic Acid.
	°C.	°C.						°C.
Original whale oil, .	Fluid	Fluid	9·50	192·2	144·8	0·27	287·7	..
Artificial tallow, .	47·5	38·1	9·88	183·7	56·9	0·25	296·4	75·5
Artificial stearine, .	54·3	47·3	7·80	187·7	11·7	0·14	297·0	74·0
Hydrogenated whale oil, . . .	41·9	31·9	5·30	190·9	57·8	0·18	282·0	76·0

In each instance the hardened fats contained nickel.

The effects of continuing the hydrogenation to its extreme limit is seen in the following examples of completely hydrogenated oil examined by *Mannich* and *Thiele*.[2]

Hydrogenated Oil.	Melting Point.	Iodine Value.	Saponification Value.	Melting Point of Insoluble Fatty Acids.
	° C.			° C.
Olive, . . .	70	0·2	190·9	71
Almond, . .	72	0·0	191·8	71
Arachis, . .	64-64·5	0·0	191·6	67
Sesamé, . .	68·5	0·7	190·6	69·5
Cacao butter, .	63·5-64	0·0	193·9	65·5
Poppy seed, . .	70·5	0·3	191·3	71
Linseed, . .	68	0·2	189·6	70·5
Tallow, . .	62	0·1	197·7	64
Lard, . . .	64	1·0	196·8	62
Cod-liver, . .	65	1·2	186·2	59

Uses of Hydrogenated Oils.—In the earlier applications of oils hardened by hydrogenation the candle industry and soap industry were first benefited, and it was only at a somewhat later stage that edible products were prepared. A hydrogenated oil intended for technical purposes was made from whale oil in Germany, and sold under the name of *candelite*.

The simplification of the hydrogenation process has led to the use of such products in place of the mixtures of oils and fats previously used for the preparation of margarine, artificial lard, and the like. Instead of mixtures of cotton-seed or similar oils with oleostearin, cotton-seed oil, or other oils, either alone or in admixture with soft

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[1] *J. Soc. Chem. Ind.*, 1914, xxxiii., 1097.

[2] *Ber. deutsch. Pharm. Ges.*, 1916, xxvi., 36.

fats, such as coconut oil, are hydrogenated until of the desired consistency for margarine. In some factories hydrogenated oils are blended with fats or oils which have not been treated by the process, but *Ellis*[1] considers that better results are obtained by using a single oil hydrogenated to the desired extent.

At one time nickel was almost invariably detected in hydrogenated fats, but in this country, at all events, steps are now taken to remove any residual traces of the catalyst, by methods such as washing the hydrogenated fat with dilute acid.

The best method of detecting nickel, when present, is by means of the dimethylglyoxime test.[2]

Hydrogenated sesamé oil examined by *Bömer*[3] yielded 0·01 per cent. of ash, containing 0·006 per cent. of nickel oxide, whilst hardened whale oil contained 0·006 per cent. of ash and 0·0045 per cent. of nickel oxide.

Offerdahl[4] found that hardened whale oil usually contained 0·5 to 2 mgms. of nickel per kilo., but from the results of feeding experiments concluded that this was of no physiological importance. Fish and marine animal oils are deodorised by hydrogenation, but the odour is liable to reappear on keeping, and in the opinion of *Klimont* and *Mayer*[5] this is the principal objection to the use of such products for margarine.

As a test for the presence of hardened fish oil they dissolve 2 to 3 grms. of the sample in 50 c.c. of acetone, and weigh the amount of deposit which is formed after 12 hours. Under these conditions oleomargarine yields 12 to 13 per cent. of crystals, melting at 45° to 47° C., whilst mixtures of oleomargarine and hydrogenated fish oil yield over 12 to 16 per cent.

The use of hydrogenated oils in the manufacture of soap has been patented by *Crosfield & Sons* (Eng. Pat. 13,042, 1907), one advantage claimed for the process being that the soap can be salted out by means of a weaker brine than usual. Soap prepared from hydrogenated oils is very much harder than that made from the ordinary untreated oil. It has been stated, however, that the soaps made from hydrogenated fats do not lather so readily as those made from the usual fats.

Another use of hydrogenated oils is in the manufacture of lubricants, and mixtures containing such products are upon the market.

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[1] *J. Soc. Chem. Ind.*, 1912, xxxi., 1165.

[2] *Knapp, Analyst*, 1913, xxxviii., 102.

[3] *Chem. Rev. Fett Ind.*, 1912, xix., 221.

[4] *Ber. deutsch. pharm. Ges.*, 1913, xxiii., 558.

[5] *Zeit. angew. Chem.*, 1914, xxvii., 645.

CHAPTER XVI.

ADULTERATION OF OILS AND FATS, ETC.: SYSTEMATIC DESCRIPTION.

THE adulteration mostly practised in the case of oils and fats, etc., may be broadly divided into two classes—viz., (1) those where some weight-giving ingredient is added *of wholly foreign nature*, as where an undue proportion of water is mechanically admixed with soft fats, such as butter and lard, or where starchy matters are added to the latter substance; and (2) those where the adulterant is a lower priced substance *of tolerably similar nature*, as where cotton-seed oil is admixed with olive oil, hemp-seed oil with linseed oil, or margarine with cow's butter.

In some cases mineral hydrocarbons (petroleum distillates) or destructive distillation oils (paraffin oils, rosin oil, etc.) are admixed with animal and vegetable oils; or substances largely consisting of unsaponifiable matters derived from wool-grease, etc., with tallow and similar saponifiable solid fats. Here the nature of the adulteration is rather of the first class than of the second, inasmuch as by appropriate processes the adulterating impurity may (to a greater or less extent) be analytically *separated from* the material examined, and directly determined quantitatively; whereas when the mixture consists of two closely similar natural oils, etc., in most cases it is difficult, if not impossible, to effect any quantitative separation of constituents whereby the extent of the admixture can be directly determined, although in many cases the fact of the admixture, and an approximate idea of its extent, can be arrived at by indirect means—*e.g.*, by the alteration in the melting point of the mixed fatty acids obtainable on saponification, or the increase (or decrease) in the iodine or saponification values; or by the production of some particular colour change with a given chemical reagent, not shown by the natural unadulterated oil, etc.

In many cases of the kind, moderate certainty can only be ensured by making comparative tests side by side with the substances examined, and with known mixtures of pure oils, etc.; and here a great difficulty is at once encountered in obtaining standard samples of pure materials. In many instances this can only be done satisfactorily by preparation of the standards in the laboratory itself—*e.g.*, by expressing hand-picked samples of seeds, etc., so as to ensure that the seeds themselves shall not be mixtures of various kinds, and the oils extracted shall be free from all adulteration. Even with all possible care in preparing pure substances for comparison, there still remains a certain amount of possibility of error, owing to the natural fluctuations brought about by differences in the soil and climate, the degree of cultivation, and similar causes. Accordingly, the analytical detection of adulteration in oils and fats, etc., not only depends for the most part on very different principles from those involved in mineral analysis —*e.g.*, for metals—but also is a matter permitting of much less quantitative certainty.

The methods adopted in testing commercial samples of oils, fats, etc., necessarily vary with each substance examined, but in general consist of a suitable selection from the various methods above described, based on the physical and chemical properties of the oils, etc. (§§ 2 and 3) ; more especially—

The physical texture, colour, taste, and odour of the substance examined.
The effect on polarised light, and the refractive index.
The specific gravity of the substance, or of the fatty acids thence obtainable.
The melting and solidifying points of these fatty acids.
The solubility in various solvents.
The efflux velocity at various temperatures.
The acid value.
The percentage of unsaponifiable matters present (including water, suspended substances, and inorganic matters).
The nature of the elaidin formed, and its degree of consistency.
In the case of drying oils, the result of tests of rate of inspissation through oxygen absorption.
The effect of qualitative reagents in producing colour reactions (nitric acid, sulphuric acid, etc.).
The degree of heat evolution on mixture with sulphuric acid and with bromine.
The nature and consistency of the product formed with sulphur chloride.
The quantitative result of Koettstorfer's test (saponification value).
,, ,, Hehner's test (insoluble acid value).
,, ,, Reichert's test (volatile acid value).
,, ,, Hübl's test (iodine value).
,, ,, Benedikt and Ulzer's test (acetyl value).
The results of various special tests applicable in certain particular cases.

The data and tests given in the following systematic description of the different oils and fats indicate the course to be followed in each case. The same system of classification is followed as in Chap. XIII., and the oils, etc., are arranged in alphabetical order in their classes.

CLASS I.—OLIVE (ALMOND CLASS).

ALMOND OIL.

Recorded Values.

Almond Oil.

Specific Gravity.	Acid Value.	Saponification Value.	Iodine Value.	Hehner Value.	Authority.
0·914-0·920	..	..	..	..	Allen.
0·9190-0·9195	..	190·5-191·2	93·5-95·5	..	De Negri and Fabris.[1]
0·9175-0·9195	..	189·5-191·7	94·1-96·5	..	„ „ [2]
0·919 at 15·5° C.	Free acid as oleic 5·13 per cent.	..	98·1	..	Sherman and Snell.
0·915-0·9211 at 15° C.	..	187·9-192	93·0-99·2	..	Dieterich.
..	..	..	..	96·2	West-Knight.
0·9178-0·9199	..	183·3-207·6	96·6-103·4	..	Lewkowitsch.

Specific Gravity.	Refractometer Reading.	Solidification Point.	Critical Temperature of Solution.	Authority.
0·915-0·9211 at 15° C.	Butyro-refractometer. 64-64·8 at 25° C.	° C. −10 to −20	° C. 32-33·5	Dieterich.
..	Oleo-refractometer. 8·0-10·5 at 22° C.	..	..	Pearmain.
..	56·5-57·0	..	..	Lewkowitsch.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
° C.	° C.		
13-14	..	93·5-95·5	De Negri and Fabris.[1]
13 14	..	94·1-96·5	„ „ [2]
14	5·14	93·5-96·3	Dieterich.
	Dalican's Test.		
..	9·5-10·1 [1]	..	Lewkowitsch.
..	11·3-11·8 [2]	..	„

Source.—Almond oil is obtained from the kernels of the sweet or bitter almond (*Prunus amygdalus*). In either case the oil is practically the same in general characteristics and chemical composition,

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[1] From sweet almonds.

[2] From bitter almonds.

though the oil from bitter almonds is stated to require a much longer time to become solid in the elaidin test.

According to *Schädler* sweet almonds contain from 45 to 55 per cent. of oil, and the bitter usually 40 to 50 per cent., but sometimes only 30 per cent.

Almond oil is chiefly used for pharmaceutical purposes, for ointments, etc.

Composition.—Almond oil contains only small quantities of the saturated fatty acids. Two specimens examined by *Hehner* and *Mitchell* gave no deposit on treating the mixed fatty acids with alcohol saturated with pure stearic acid.

The liquid fatty acids appear to consist mainly of oleic acid with a small quantity of linolic acid. *Farnsteiner*[1] separated linolic tetrabromide (m.p. 113° to 114° C.) in a proportion corresponding to 5·97 per cent. of linolic acid.

Hehner and *Mitchell*[2] have shown that almond oil does not yield any insoluble bromide of a mixed glyceride, and that the mixed fatty acids do not give linolenic hexabromide.

Ethyl Esters of Almond Fatty Acids.—*Henriques*[3] prepared these by partially saponifying almond oil with alcoholic alkali, and distilling the esters in a current of superheated steam. They had the following constants:—Saponification value, 185·0; mol. equivalent, 302·7; acid value of liberated acids, 204·6; mol. equivalent of acids, 273·7; and iodine value, 91·1.

Properties and Tests of Purity.—Almond oil is pale yellow, and very fluid. It has a bland taste recalling that of the almond, but it is very liable to become rancid. It is said to be less digestible than olive oil, and in large doses to have a purgative effect.

Absorption Spectrum.—*Allen* considers that this may furnish evidence of adulteration, since almond oil, unlike most vegetable oils, gives a spectrum without bands or pronounced absorption in the red or violet parts.

Solidification Point.—According to *Schädler*, almond oil thickens at − 10° C., becomes turbid at − 16° C., and solidifies to a white mass at − 20° C. A specimen examined by the present writer (*M.*) became turbid at − 10° C., but did not solidify at − 18° C. By chilling the oil in this way it is possible to detect the presence of olive oil or lard oil.

Saponification Value.—In addition to the figures given in the table of constants, the following values have been recorded:—195·4 (*Valenta*), and 187·9 (*Peters*). Any considerable addition of rape oil will lower this value.

Iodine Value.—Other recorded values are:—98·4 (*Hübl*), 98 to 99 (*Peters*), and 96·6 (*Mitchell*). This constant will afford indication of the adulteration of almond oil with cotton-seed, sesamé, poppy-seed, or walnut oils.

Bromine Values.—*Vulté* and *Logan*[4] obtained the following results with almond oil, the iodine value being determined by Hübl's method, and the bromine values by M'Ilhiney's method:—

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[1] *Zeit. Unters. Nahr. Genussm.*, 1899, ii., 1 to 27.

[2] *Analyst*, 1898, xxiii., 314.

[3] *Zeit. angew. Chem.*, 1898, 338.

[4] *J. Amer. Chem. Soc.*, 1901, xxiii., 156.

Iodine Value. (*Hübl*).	Iodine Value Calculated from Bromine.	Total Bromine Absorption.	Bromine Addition.	Bromine ubstitution.
89·64-90·53	89·64-90·20	59·34	57·20	2·14

The Bromine Thermal Value is very closely proportional to the iodine value, and almond oil is one of the best oils on which to standardise the vacuum-jacketed tubes.

Valenta's Test.—*Chattaway*, *Pearmain*, and *Moor*[1] obtained results ranging from 72° to 87° C. with five samples of almond oil.

Solubility of the Fatty Acids.—The German Pharmacopæia requires that almond oil fatty acids shall dissolve in an equal volume of alcohol at 15° C., and that the solution shall remain clear on the addition of twice that amount of alcohol.

Since olive, earth-nut, cotton-seed, and sesamé oil contain considerably more solid fatty acids than almond oil, their presence may be detected by this test.

Critical Temperature of Solution.—This is considerably lower than the values obtained with peach-kernel and apricot-kernel oil. Thus, *Dieterich* gives the following figures:—Almond oil, 32° to 33·5° C.; apricot-kernel oil, 46° to 47° C.; and peach-kernel oil, 41° C.

Maumené Test.—The following values have been obtained by the older method:—52° to 54° (*Maumené*), 51° to 53° (*De Negri* and *Fabris*). The halogen standard figure (*Mitchell*) is proportional to the iodine value.

Detection of Adulteration.—*Cotton-seed*, *sesamé*, *olive*, *poppy*, *earth-nut*, and *rape oils* can be detected by the variations they produce in the normal constants of almond oil, and the two first by Halphen's and Baudouin's colour reactions. The determination of arachidic acid affords information of the presence of earth-nut oil.

Apricot, *plum*, and *peach-kernel oils* are also extensively used for adulterating almond oil, and as their physical and chemical characteristics are very similar to those of almond oil, it is very difficult to detect the addition.

Various colour reactions have been proposed. Thus *Micko*[2] recommends the use of *nitric acid* of 1·4 specific gravity, which gives a pale yellow colour with almond oil, and an orange colour with plum-, apricot-, or peach-kernel oils.

Bieber's Test.[3]—The oil is shaken with five times its volume of a mixture in equal parts by weight of concentrated sulphuric acid, fuming nitric acid, and water. According to *Bieber*, the following results are obtained:—

Almond Oil.—Pale yellow mass, changing to red.

Peach-kernel Oil.—Immediate peach coloration, changing to dark orange.

Sesamé Oil.—Pale yellowish-red, changing to dull orange-red.

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[1] *Analyst*, 1894, xix., 150.

[2] *Analyst*, 1893, xviii., 149.

[3] *Zeit. anal. Chem.*, 1878, xvii., 264.

Poppy and *Walnut Oils.*—Mass somewhat whiter than that given by almond oil.

Dieterich[1] gives the following comparative results :—

	Almond Oil.	Peach-kernel Oil (fresh).	Apricot-kernel Oil (fresh).
Nitric acid, ...	pale yellow mass,	red, . .	yellow mass.
Sulphuric acid, . .	red, then black,	red, then black.	red, then black.
Molybdic acid, with H_2SO_4. . .	yellowish, .	black, . .	red to reddish-brown.
Nickle's reaction (emulsion with $Ca(OH)_2$),	emulsion soon clear, . .	not sharp, . .	emulsion remaining.
$H_2SO_4 + HNO_3$ (equal parts), . .	faint yellow, .	red colour, .	red colour.
Elaidin test, . .	white solid mass,	yellow mass, .	yellow mass.

A determination of the critical temperature of solution should also furnish an indication of the presence of peach-kernel or apricot-kernel oil.

The following results given by *Lewkowitsch*[2] show the slight differences between the analytical values for these similar oils :—

Oil.	Specific Gravity.	Saponification Value.	Iodine Value.	Butyro-refractometer at 40° C.	Free Fatty Acids.	Fatty Acids.		Bieber's Test.
						Neutralisation Value.	Soponification Value.	
Almond oils expressed from								
1. Valencia sweets, .	0·91995	207·6	99·4	57·5	2·61	207·8	207·6	Colourless.
2. Blanched Valencia sweets, . .	0·9182	191·7	103·4	57·5	1·46	196·4	201·7	,,
3. Sicily sweets, . .	0·9178	183·3	100·3	57·0	0·39	198·8	202·2	,,
4. Mazagan bitters, .	0·9180	188·6	102·5	56·5	1·56	196·8	203·1	,,
5. Small Indian almonds, . .	0·9190	189·2	96·6	57·0	1·46	195·8	200·7	,,
6. Mogador bitters, .	0·9183	194·9	104·2	57·0	0·65	197·1	203·2	,,
7. Peach-kernel oil, .	0·9198	191·4	95·24	57·5	1·51	196·8	205·0	Colourless at first, then pink.
8. Apricot-kernel oil, .	0·9200	192·4	107·4	58·0	1·16	198·0	202·0	Pink.
9. Apricot-kernel oil (Mogador kernels),	0·9172	198·2	107·9	57·0	1·41	194·0	200·7	Slightly pink.
10. Californian apricot-kernel oil, . .	0·92026	190·3	108·7	58·0	0·61	197·8	202·8	Very slight pink.

It has been found by *Ross* and *Race*[3] that the chromogenic constituent in apricot-kernel oil is not volatile with steam, and that even after steaming for several hours, or blowing air through the oil, it still gives a pronounced reaction in Bieber's test.

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[1] *Chem. Rev. Fett Ind.*, 1901, viii., 210.

[2] *Analyst*, 1904, xxix., 106.

[3] *Analyst*, 1911, xxxvi., 263.

APRICOT-KERNEL OIL.

Recorded Values.

Apricot-kernel Oil.

Specific Gravity.	Acid Value.	Saponification Value.	Iodine Value.	Critical Temp. of Solution.	Butyro-Refractometer.	Solidification Point.	Authority.
				°C.		°C.	
..	..	192·2 to 192·9	101	..	..	..	De Negri and Fabris.
0·915 at 15° C.,	..	..	..	..	..	−14	Schädler.
0·9211 „	0·64	193·11	108·07	..	..	..	Micko.[1]
0·915 to 0·9211 at 15° C., 0·9010to0·9018 at 90° C.,	3·52 to 3·60	193·1 to 215·1	100 to 108·67	46 to 47	65·5 to 67 at 25° C. 58·0 at 40° C. 52·25 at 50° C.	−14 to −20	Dieterich.[2]
0·9195 at 15°C.	12·14	188·0	96·0	..	56·3 (=1·4634)	..	Crossley & Le Sueur.[3]
0·9172-0·9200	..	191·4 to 198·2	107·4 to 108·7	..	58·0 at 40° C.	..	Lewkowitsch.

Fatty Acids.

Specific Gravity.	Melting Point.	Solidification Point.	Saponification Value.	Iodine Value.	Butyro-Refractometer.	Critical Temp. of Solution.	Authority.
	°C.	°C.					
0·9095 at 15° C., 0·8875 at 90° C.,	4·5	0·0	...	99·06 to 99·82	50 25 to 56 5 at 25° C.	19·5	Dieterich.
...	2·3 to 3·5	...	...	103·8	...	...	De Negri and Fabris.
...	13·4 to 14[4]	...	194·04	102·64	..	...	Micko.

This oil is expressed from the kernels of the apricot, *Prunus armeniaca*, which contain from 40 to 41 per cent.

It is of a pale yellow colour and closely resembles almond oil in its chemical and physical characteristics, the chief difference being that the iodine value and critical temperature of solution are somewhat higher.

For the colour tests that have been recommended for the detection of apricot-kernel oil, see *Almond Oil.*

According to *De Negri* and *Fabris*,[5] Nickle's reaction is the best means of detecting apricot-kernel oil. On shaking the oil with slaked lime, a permanent emulsion is obtained with apricot-kernel oil, whilst olive, almond, and rape oils remain clear. It is stated that an addition of 10 per cent. of apricot-kernel oil to almond oil can thus be

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[1] *Analyst*, 1893, xviii., 149.

[2] *Chem. Rev. Fett Ind.*, 1901, viii., 210.

[3] *J. Soc. Chem. Ind.*, 1898, xvii., 992.

[4] Capillary tube method.

[5] *Zeit. anal. Chem.*, 1894, xxxiii., 557.

detected. Peach-kernel oil also gives the reaction, though not so sharply as apricot-kernel oil.

BEN OIL.

This oil is expressed from the seeds of *Moringa oleifera*, which is indigenous to Egypt, Arabia, Syria, and the East Indies, and has been cultivated for many years in tropical America.

The kernels yield about 25 per cent. of a white or pale yellow oil, with a slightly sweet taste. It does not readily become rancid. It consists of the glycerides of stearic, palmitic, and oleic acids, and also, according to *Völker*, of behenic acid. The phytosterol separated by *Van Itallie* melted at 131° to 135° C.

Schadler [1] states that it becomes viscid at 15° C. and turbid at 7° C., and then begins to yield a solid deposit. It solidifies completely at 0° C. Its specific gravity at 15° C. is 0·9120.

Lewkowitsch recorded the following values:—Specific gravity, 0·91267 to 0·91998; solidification point, 8·8° C.; saponification value, 184·6 to 187·7; iodine value, 109·9 to 112·6; and butyro-refractometer reading, 50·0 to 60·5.

At one time this oil was extensively employed for cosmetic purposes, in the manufacture of toilet soaps, and especially as a medium for the extraction of delicate perfumes, such as violet, from flowers.

That portion of the oil which remains fluid at + 7° C. is a valuable lubricant for delicate machinery, clocks, etc.

CANDLE-NUT OIL.

Recorded Values.

Candle-Nut Oil.

Specific Gravity.	Saponification Value.	Hehner Value.	Iodine Value.	Acetyl Value.	Butyro-Refractometer.	Solidification Point.	Authority.
0·920-0·926 at 15° C.	184 to 187·36	..	136·3 to 139·3	..	75·5-76 at 15° C.	Fluid at –18° C.	De Negri[2]
..	..	94·56	118	..	..	..	Lach.[3]
0·92565 at 15·5° C.	192·6	95·5	163·7	9·8	76 at 25° C. 78·5 at 28° C.	..	Lewkowitsch.[4]
0·9232	..	..	..	..	..	..	Cloez.
..	109·3	..	164·0	..	65·7 at 40° C.	..	Bolton & Revis.[5]
..	202·5	..	148·8	..	..	..	Bolton & Revis.[6]

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[1] *Technologie der Fette*, 523.

[2] *Chem. Centralbl.*, 1898, ii., 493.

[3] *Chem. Zeit.*, 1890, xiv., 871.

[4] *Chem. Rev. Fett Ind.*, 1901, viii., 156.

[5] *A. moluccana.*

[6] *A. triloba.*

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
°C.	°C.		
20·21	13	142·7-144·1	De Negri.
65·5	56	..	Lach.

Source.—Candle-nut oil is obtained from the kernels of the nuts of the candle-nut tree, *Aleurites moluccana*, which yield from 58 to 60 per cent. of oil on extraction with a suitable solvent.

The cold expressed oil is clear and nearly colourless, whilst the hot pressed oil is brown, and has an unpleasant odour and flavour.

Composition.—Its elementary composition is given by *Schädler* as :—Carbon, 76·72 ; hydrogen, 11·36 ; and oxygen, 11·92.

It contains the glycerides of oleic, linolic (about 30 per cent.), stearic, palmitic, and myristic acids, and, judging by its marked drying properties, linolenic acid is not improbably present.

Properties.—It readily becomes rancid, and develops a large amount of acidity. Thus a specimen of the oil examined by *Noerdlinger* contained 56·5 of free fatty acid. Oxidation changes probably account for the differences in the recorded chemical and physical constants. It yields a considerable quantity of insoluble bromide in the bromine test (*e.g.*, 7·28 to 8·21 per cent).[1]

When boiled it produces a varnish which dries with great rapidity, excelling boiled linseed in this respect. The soap resembles that made from coconut oil, and the oil can take the place of that fat in many soaps.

With Baudouin's reagent it gives no coloration ; but, according to *De Negri*, the oil extracted with ether gives a faint brown tinge in Becchi's test, whilst that extracted with petroleum spirit gives an intense brown coloration.

Schädler states that candle-nut oil is sometimes used to adulterate olive oil, though as the oil has purgative properties, like castor oil, it cannot be extensively used for this purpose. Any large addition would tend to raise the specific gravity and iodine value of the olive oil.

The oil examined by *Lach* (*supra*) was probably obtained from a different species of *Aleurites*, since the values differ so widely from those of other observers. It agrees somewhat more closely with the values of the oil from *A. triloba*, which has a pleasant odour and taste, and is used for food purposes. Chinese wood oil is obtained from another species of *Aleurites*.

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[1] Walker and Warburton, *Analyst*, 1902, xxvii., 237.

CARAPA OIL.

CRAB OIL. ANDIROBA OIL.

Recorded Values.

Carapa Oil.

Specific Gravity.	Acid Value.	Saponification Value.	Hehner Value.	Bromine Value.	Solidification Point.	Authority.
At 15·5° C.					C.	
0·9225	22·6	195·6	93·7	41 = I. value 65	4·5	Deering.[1]
0·912	...	...	95·5	...	30·7	,, [2]

Fatty Acids.

Melting Point.	Solidification Point.	Authority
° C.	C.	
38·8	...	Deering.
...	56·4	...

Carapa oil is extracted from the nuts of *Carapa guianensis*, a tree indigenous to the West Indies and Central America. The nuts yield about 70 per cent. of oil, which is used locally as a preservative for timber.

According to *Deering* it is a yellow, non-drying liquid, with an intensely bitter taste, whence its name of crab oil. When chilled it solidifies to a tallow-like mass. Its viscosity at 70° F. is about the same as that of rape oil.

The specimen examined by *Deering* contained 10·4 per cent. of glycerol, about 12 per cent. of free fatty acids, and volatile fatty acids equivalent to 0·25 per cent. of potassium hydroxide.

It was found to yield a good soap resembling olive oil soap in character.

The other specimen was evidently a different substance from Deering's oil. It was a white solid resembling beef-suet in appearance. It contained 51 per cent. of solid fatty acids consisting of four-fifths of stearic acid and one-fifth of palmitic acid.

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[1] Deering, *Imp. Inst. J.*, 1898, 313.

[2] *Rev. Chim. Ind.*, 1900, xiii., 116.

CHAULMOOGRA OIL.

Recorded Values.

Chaulmoogra Oil.

	Specific Gravity.	Specific Rotation in $CHCl_3$ for Adam Light.	Acid Value.	Saponification Value.	Iodine Value.	Authority.
Max., .	0·9535	+58·20	21·48	210·5	110·4	Brill and Williams.
Min., .	0·9429	+45·69	1·55	189·1	97·6	,,
Mean, .	0·9471	+50·81	0·79	200·4	102·4	,,
	0·951 at 25° C.	+52·0	23·9	213	103·2	Power.
	0·9488 at 30° C.	..	11·18 per cent. (as oleic)	226·83	96·5	Chattopadhyay.

Fatty Acids.

Specific Rotation.	Melting Point.	Iodine Value.	Solidification Point.	
+54·00 and +47·0	38-40	99·7-101·3	..	Brill and Williams.
			37·3	Chattopadhyay.

Chaulmoogra oil is obtained by extracting the seeds of an Indian plant, Chaulmoogra, *Taraktogenos Kurzii*, with a suitable solvent, the yield being about 53 per cent., calculated on the dry kernel. It is used medicinally, having properties not possessed by hydnocarpus oil, which is not infrequently sold as chaulmoogra oil.

Oil extracted by *Brill* and *Williams*[1] from the seeds of *Hydnocarpus anthelmintica* (Madras) had the following characters:—Specific gravity at 30°, 0·9487; specific rotation, + 49·50; acid value, 0·6; saponification value, 206·2; and iodine value, 90·8.

The active principle of chaulmoogra oil is *gynocardin*, ($C_{13}H_{19}O_9N + 1·5\ H_2O$). Eight samples of chaulmoogra oil examined by Brill and Williams contained 0·00438 to 0·2209 per cent. of nitrogen, corresponding with 0·113 to 0·568 per cent. of gynocardin.

Chaulmoogric and hydnocarpic acids isolated by *Brill* and *Williams* (*loc. cit.*) from the mixed fatty acids had the following values:—

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[1] *Philippine Journ. Sci.*, 1917, xii., 207.

	Neutralisative Value.	Specific Rotation.	Iodine Value.
Chaulmoogric acid, .	200·5 and 202·4	+59·05 and 58·10	89·5 and 90·7
Hydnocarpic acid, .	222·7 and 218·2	+67·70 and 67·60	100·2 and 99·9

Chaulmoogric acid is a representative of a new series of fatty acids having the general formula $C_nH_{2n-4}O_2$, and possessing a cyclic structure. See also *Power* and *Barrowcliffe*.[1]

Chattopadhyay[2] isolated an oil from seeds of *Taraktogenos Kurzii*, which remained liquid at 15° C. It consisted of glycerides of lauric, chaulmoogric, and linolic acids. Some of the values recorded by *Chattopadhyay* (see table above) are abnormal, and doubt has, therefore, been thrown upon the purity of the seeds extracted by him.

CHERRY-KERNEL OIL.

Recorded Values.

Oil.

Specific Gravity.	Acid Value.	Saponification Value.	Iodine Value.	Maumené Test.	Solidification Point.	Authority.
At 15° C.				° C.	° C	
0·9285	1·11	193·36	114·3	...	...	Micko.
0·9234-0·9238	...	195	110	45	− 19 to − 20	De Negri & Fabris
0·9184	...	...	...	...	− 19 to − 20	Schädler.

Fatty Acids.

Melting Point.	Solidification Point.	Saponification Value.	Iodine Value.	Mean Molecular Weight.	Authority.
° C.	° C.				
16·0-20·6	...	189·04	104·33	296·23	Micko.
19-21	13-15	...	114·3	...	De Negri & Fabris.

This oil is obtained from the kernels of the fruit of the cherry tree (*Prunus cerasus*). It has a slight odour of almonds, and, according to *De Negri* and *Fabris*, contains an appreciable quantity of hydrocyanic acid.

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[1] *J. Chem. Soc.*, 1905, lxxxvii., 349; 1910, xcvii., 1285.

[2] *Amer. J. Pharm.*, 1915, lxxxvii., 473.

In some parts of South Germany it is used for culinary, burning, and lubricating purposes. It gives a faint brown coloration with Becchi's reagent. When treated with nitric acid (sp. gr. 1·4) it gives a dark reddish-brown colour, and on standing the acid layer becomes bright red. With Bieber's reagent a brown colour, which darkens on standing, is obtained.

Cherry-kernel oil is sometimes employed to adulterate almond oil.

COFFEE-BERRY OIL.

Recorded Values.

Coffee-Berry Oil.

Specific Gravity.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index at 25° C.	Maumené Test	Solidification Point.	Authority.
					° C.	° C.	
0·951-0·952	165-173	79-87	...	...	37-41	3-6	De Negri and Fabris.[1]
...	176-177	...	1·65-1·7	1·4777 to 1·4778	...	...	Spaeth.[2]
				Butyro-refractometer.			
...	...	...	...	79-79·25	...	...	„

Fatty Acids.

Melting Point.	Solidification Point.	Saponification Value.	Iodine Value.	Authority.
° C.	° C.			
37-41	34-36	172-178	88·8-90·3	De Negri and Fabris.

Coffee-berries contain from 8 to 14 per cent. of oil, which can be extracted by means of solvents. The oil thus obtained is brownish-green in colour, and has a faint odour of the berry.

The oil extracted by *Spaeth* contained 2·25 to 2·29 per cent. of free fatty acids in terms of oleic acid.

Hilger and *Juckenack*[3] found that the loss of fat during the roasting of coffee was 9 to 10 per cent. As a rule, the different constants of the fat showed an increase after the roasting.

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[1] *Zeit. anal. Chem.*, 1894, xxxiii., 569.

[2] *Chem. Zeit.*, 1895, [Rep.], 252.

[3] *Forschungs Ber.*, 1897, iv., 119.

ARACHIS OIL (EARTH-NUT OIL, PEA-NUT OIL).

Recorded Values.

Oil.

Origin.	Specific Gravity.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Authority.
		Free Acid as Oleic. Per cent.					
Virginian nuts, . .	0·917 at 15° C.	0·55	192·53	91·75	0·48	94·87	Sadtler.
Spanish ,, . .	0·9175 ,,	0·79	190·68	94·77	1·60	95·31	,,
African ,, . .	0·911	0·62	194	85·6	...	...	,,
Puducheri, . . .	0·920	...	193·1	95	...	...	,,
Commercial, . . .	0·9209	6·20	192·1	98·4	...	95·86	,,
,, . . .	0·917	...	190·2	95-95·4	...	...	De Negri and Fabris.
American. . . .	0·9136 at 24° C.	...	...	92·51	...	...	Merrill.
,, from roasted nuts.	0·9142 ,,	...	...	92·37	...	...	,,
,, ,,	0·922	...	...	...	...	...	Allen.
,, ,,	0·918 -0·9202	...	194-196	...	...	...	Schädler.
Madras (4), . . .	0·9195-0·9256	1·45-6·80	185·6-194·8	92·43-100·82	0·00	95·63	Crossley and Le Sueur.[1]
American (4), . . .	...	...	185·5-191	...	...	...	Lane.

Fatty Acids.

Origin.	Specific Gravity	Melting Point.	Solidification Point.	Iodine Value.	Mean Molecular Weight.	Authority.
		° C.	° C.			
Various nuts, . .	...	29-34	25-32·5	...	...	Sadtler.
Commercial, . . .	0·846 at 99° C. (Water at 15·5°C.=1)	27·8-29·5	28	...	281·8	Allen.
Pondichéry nuts, . .	...	29-31	25-23	...	...	De Negri and Fabris.
Coromandel ,, . .	...	28-30	25-22	103·42	...	,, ,,
Commercial, . . .	...	26-27	25-23	96-97	...	Schädler.
				Liquid Fatty Acids.		
American (4), . .	...	...	...	128·5	...	Wallenstein and Fink.
...	...	...	...	111-119·5	...	Lane.
Chinese, . . .	...	...	...	131·0	...	,,

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[1] *J. Soc. Chem. Ind.*, 1898, xvii., 992.

Source.—Earth-nut oil is obtained from the seeds of *Arachis hypogœa*, in which it is present to the extent of about 50 per cent. It is extensively cultivated in Virginia, various parts of India, and in Africa. During the last few years there has been a considerable diminution in the exports of seed from India, and, in particular, from Madras, mainly on account of bad seasons, but also to some extent from poorer crops, through deterioration of the soil. The output from Virginia has also been smaller from the same causes, so that African nuts have formed the chief source of much of the oil expressed at Havre and Marseilles.

The earth-nut is also extensively grown in China, especially where there is a sandy soil like that of Chefoo. The nuts are roasted, rolled, winnowed, gleaned, and pressed, and the oil is used for burning and as a food.

Expression.—The nuts contain upwards of 50 per cent. of oil. According to *Sadtler* Virginian nuts yield about 38 per cent. of oil on cold expression, and an additional 10 per cent. with hot pressure.

The cold-drawn oil is very pale yellow, and is largely used for edible purposes. It is less liable than olive oil to become rancid. The second and subsequent yields are used for lubricating purposes, and in the manufacture of Castile soap, of which a large quantity is made at Marseilles from the oil of African nuts.

According to *Schädler*[1] the oil obtained from the nuts forms three grades in the following proportion:—First pressing, consisting of the finest salad oil = 16 to 18 per cent.; second pressing, salad and lamp oil = 7 to 8 per cent.; and third pressing, lubricating oil = 7 to 8 per cent. The residual oil-cake contains about 8·5 per cent. of oil, and the loss amounts to about 1·5 per cent.

Composition.—Earth-nut oil contains palmitin, stearin, arachidin, lignocerin, olein, linolin, and probably hypogæin.

There has been considerable discussion as to the presence of hypogæic acid, which was stated by *Gössmann* and *Scheven*[2] to be a constituent of the liquid fatty acids, but was not found by *Schoen*.[3] *Hazura*,[4] however, considered its occurrence as not improbable.

Hehner and *Mitchell*[5] obtained, by their method of estimating stearic acid, 7 per cent. of a deposit melting at 67° C. from the mixed fatty acids. *Kreiling*[6] showed that the insoluble fatty acids which were originally regarded as arachidic acid were really a mixture of lignoceric and arachidic acids in which the former predominated (*vide infra*).

Farnsteiner[7] separated about 30 per cent. of unsaturated fatty acids, about 6 per cent. of which consisted of linolic acid.

Properties and Tests of Purity—*Specific Gravity.*—The highest recorded value is 0·9236 at 15° C. (*Crossley* and *Le Sueur*); the lowest,

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[1] *Technologie der Fette*, i., 518.

[2] Liebig's *Annalen*, xciv., 230.

[3] *Ber.*, xxi., 878.

[4] *Wiener Monatshefte*, x., 242.

[5] *Analyst*, 1896, xxi., 328.

[6] *Ber. d. d. chem. Ges.*, xxi., 880.

[7] *Zeit. Untersuch. Nahr. Genussm.*, 1899, ii., 1.

0·911 at 15° C. for African oil (*Sadtler*). The ordinary figures are practically the same as those of olive oil.

Schädler states that the finest oil has a specific gravity of 0·918 at 15° C., whilst older oil, or that obtained by hot expression, has a density of 0·9202 at the same temperature.

Solidification Point.—*Sadtler*[1] made the following observations:—Virginian oil, + 3° C.; Spanish oil, + 3° C.; African oil, + 2° C.; and commercial oil, + 10° C.

According to *Schädler* earth-nut oil becomes turbid at + 3° C., congeals at — 3° to — 4° C., and completely solidifies at — 7° C.

Iodine and Bromine Values.—The highest figures obtained for the Hübl value are 101 to 105 (*Oliveri*); the lowest, 85·6 (*Sadtler*, *Schoen*).

Wijs[2] obtained a value of 87·25 by his own method, and of 87·26 by Hübl's method.

The bromine thermal value of earth-nut oil is proportional to the iodine value, and affords a rapid method of arriving at that constant. Earth-nut oil does not yield any insoluble derivative on treatment with bromine.

Heat of Combustion.—*Merrill*[3] found the heat of combustion of samples of American oil from raw and roasted nuts to be 9,750 and 9,577 calories per gramme respectively.

Maumené Test.—The following figures have been obtained by the older method:—67 (*Maumené*); 45·5 to 49 (*De Negri* and *Fabris*); specific temperature reaction, 105 and 137 (*Thomson* and *Ballantyne*).

The writer has shown that the iodine value calculated from the Maumené figure of the fatty acid is in close agreement with that calculated from the bromine thermal rise (*cf. Maumené Test*).

Drying Properties.—Earth-nut oil is superior to olive oil in its drying properties, but inferior to cotton-seed or sesamé oil. *Bishop*[4] found that samples mixed with manganese resinate and powdered silica gained in weight from 6·50 to 6·70 per cent.

Solubility in different Solvents.—Earth-nut oil is readily soluble in ether, chloroform, and carbon tetrachloride. It dissolves to the extent of 0·52 per cent. in alcohol (90 per cent.).

In the *Valenta test* the following figures have been recorded:—112 (*Valenta*); 87 (*Allen*); 72 to 92 (*Hurst*); 72·0 to 73·5, with acetic acid 99·5 per cent. (*Chattaway*, *Pearmain*, and *Moor*); 76·0, with acid of specific gravity 1,054·2; 96, with acid of specific gravity 1,055·2; and 112, with acid of specific gravity 1,056·2 (*Thomson* and *Ballantyne*).

The *critical temperature of solution* in 90 per cent. alcohol was found by *Crismer* to be 123° C.

Refractometer Reading.—A specimen of Madras oil gave a reading of 57·5° in the Zeiss butyro-refractometer at 40° C., which corresponds with the refractive index 1·4642 (*Crossley* and *Le Sueur*).

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[1] *Amer. J. Pharm.*, 1897, lxix., 490.

[2] *Ber. d. d. chem. Ges.*, 1898, xxxi., 750.

[3] *Maine Agric. Exper. Stat. Bull.*, 1900, [65], iii.

[4] *J. Pharm. Chim.*, 1896, 55.

Procter[1] obtained the following values:—Refractive index at 15° C. = 1·4731; at 60° C. = 1·4564. Specific refraction, $R_G = \frac{n-1}{d}$ = 0·5136 at 15° C.; 0·5127 at 60° C.; and specific refraction, $R_L = \frac{n_2 - 1}{d(n_2 + 2)}$ at 15° C. = 0·3046; at 60° C. = 0·3057.

With American earth-nut oil *Merrill*[2] obtained a reading of 1·4701, and with oil from roasted nuts a reading of 1·4697 at 24° C.

The average reading of five samples examined by *Pearmain*[3] in Amagat and Jean's oleo-refractometer was + 6·0.

The Detection of Arachis Oil in other Oils.

Colour Reaction.—*Van Engelen*[4] shakes 5 c.c. of the oil with five or six drops of a solution of 0·25 gramme of sodium molybdate in 20 c.c. of sulphuric acid. Earth-nut oil gives a violet-purple colour, fading after about a minute, whilst olive oil gives a brown coloration. The test did not give satisfactory results in the case of mixtures of earth-nut and olive oils, and so can only be regarded as useful in affording evidence of the identity of the former when by itself. The colours given by other oils were—sesamé, dark brown; cotton-seed, black; and poppy, lilac.

Quantitative Methods.—The iodine value and other constants will often furnish evidence of the presence of certain oils, such as fish oils used to adulterate earth-nut oil; but the most valuable test of its presence—*e.g.*, in olive oil—is based on the determination of the arachidic and lignoceric acid which it contains to the extent of about 5 per cent. No other commonly-occurring oils, with the exception of rape-seed oil, mustard-seed oil, and certain varieties of olive oil, contain more than insignificant amounts of those acids.

Renard's Process.—*Renard*,[5] who was the first to describe this test, dissolved the fatty acids from 10 grammes of the oil in 50 c.c. of 90 per cent. alcohol and treated the solution with lead acetate. The precipitate of lead soap was shaken with ether to dissolve out the lead oleate, etc., and the residual lead salts decomposed with hot dilute hydrochloric acid. The fatty acids were dissolved in five parts of hot alcohol, from which on cooling crystals of arachidic acid were deposited when earth-nut oil was present in the original oil. The weight of these, with the addition of a correction for solubility (*vide infra*), gives an approximate idea of the amount of earth-nut oil, on the assumption that oil contains on the average 5 per cent. of arachidic acid.

It was shown by *Kreiling*[6] that the deposit which Renard regarded

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[1] *J. Soc. Chem. Ind.*, 1898, xvii., 1023.

[2] *Maine Agric. Exper. Stat. Bull.*, 1900, [65], 111.

[3] *Analyst*, 1894, xix., 134.

[4] *Bull. de l'Ass. belge Chim.*, 1896, x., 161.

[5] *Comptes Rendus*, lxxiii., 1330.

[6] *Ber.*, 1888, xxi., 880.

as arachidic acid contained also an acid of higher melting point (81° C.), lignoceric acid.

Archbutt[1] found the mixed acids thus obtained from a specimen of oil to have a molecular equivalent corresponding with 73·6 per cent. of lignoceric acid and 26·4 per cent. of arachidic acid.

Kreis[2] modified Renard's process by taking 20 grammes of oil, and using an alcoholic solution of lead acetate for the precipitation.

De Negri and *Fabris*[3] examined different experimental mixtures of olive and earth-nut oil by Renard's process, and from their results it appears that not more than 10 per cent. of earth-nut oil can be detected in a mixture when only 10 grammes are taken.

Tortelli and *Ruggeri*[4] have devised the following modification of the process, which they show to be capable of estimating the oil within 1 or 2 per cent. of a known quantity:—20 grammes of the oil are saponified, and the soap solution exactly neutralised and poured in a thin stream into a hot solution of lead acetate (50 c.c. of a 10 per cent. solution with 250 c.c. of water). The resulting lead soap is washed, dried on filter paper, and heated for about twenty minutes with anhydrous ether under a reflux condenser. The insoluble salts are washed with ether and the fatty acids liberated. The ethereal solution is washed with water, filtered, and the ether evaporated. The residue is dissolved in 100 c.c. of 90 per cent. alcohol in a stoppered flask, which is gently warmed. If earth-nut oil was present in the original oil to the extent of 5 per cent., a deposit consisting of a mixture of needle-shaped crystals (lignoceric acid) and thin tabular crystals (arachidic acid) is obtained.

The temperature at which crystallisation commences gives an approximate idea of the proportion of earth-nut oil originally present, as is shown in the following table:—

Solution in 100 c.c. of 90 per cent. Alcohol at about 60° C.								
	°C.	°C.	°C.	°C.	°C	°C.	°C.	°C.
Temperature of incipient crystallisation,	35-38	31-33	28-30	25-26	22-24	20·5-21·5	18-20	16-17
Per cent. of earth-nut oil in the mixture,	100	60	50	40	30	20	10	5

In more exact estimations, the precipitate formed in the alcohol. after standing for three hours at 15° to 20° C., is collected on a filter and washed with three successive portions of 10 c.c. of 90 per cent. alcohol, and then with 70 per cent. alcohol. It is next dissolved in boiling absolute alcohol, and the residue left on evaporating the latter

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[1] *J. Soc. Chem. Ind.*, 1898, xvii., 1124.

[2] *Chem. Zeit.*, 1895, xix., 451.

[3] *Zeit. anal. Chem.*, 1894, xxxiii., 552.

[4] *Chem. Zeit.*, 1898, xxii., 600.

recrystallised from 90 per cent. alcohol. The new precipitate is treated as before and finally dissolved off the filter by means of boiling absolute alcohol, the solution evaporated in a weighed basin, and the residue dried at 100° C. and weighed. In this way a mixture of lignoceric and arachidic acids melting at 74° to 75·5° C. is obtained, and from the weight of residue, plus the amount dissolved by the alcohol, the percentage of earth-nut oil in the mixture can be calculated.

The following table gives the correction experimentally determined for a mixture of these acids melting at 74° to 75·5° C. :—

Weight of Mixed Acids.	100 c.c. of 90 per cent. Alcohol dissolve at		
	T = 15° C.	T = 17·5° C.	T = 20° C.
	Gramme.	Gramme.	Gramme.
1 between 2·7 and 0·50 gramme,	0·079	0·080	0·090
2 ,, 0·47 ,, 0·17 ,,	0·050	0·060	0·070
3 ,, 0·11 ,, less, . .	0·033	0·040	0·045

The amounts of the mixed acids present in earth-nut oil were found to vary from 4·30 to 5·40 per cent., the mean being about 4·80 per cent.

In Renard's original process and its modifications, the coefficient of solubility for the "arachidic acid" in 90 per cent. alcohol is taken as 0·022 gramme at 15° C. and 0·045 gramme at 25° C., but in the light of the above determinations these corrections are evidently too small.

Archbutt[1] confirms the general correctness of Tortelli and Ruggeri's results, but gives the following table of corrections as being more accurate :—

Weight of Fatty Acids Obtained.	Corrections per 100 c.c. of 90 per cent. Alcohol for Crystallisation and Washing.		
	15° C.	17·5° C.	20° C.
0·1 or less	+ 0·033	+ 0·039	+ 0·046
0·2 ,,	0·048	0·056	0·064
0·3 ,,	0·055	0·064	0·074
0·4 ,,	0·061	0·070	0·080
0·5 ,,	0·064	0·074	0·085
0·6 ,,	0·067	0·077	0·088
0·7 ,,	0·069	0·079	0·090
0·8 ,,	0·070	0·080	0·091
0·9 and upwards	0·071	0·081	0·091

In Archbutt's opinion, it is a mistake to neutralise the original soap solution with acetic acid, and he shows that the most accurate and rapid method is fractionally to precipitate the free fatty acids, using only 1 gramme of lead acetate for each 10 grammes of oil taken.

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[1] *J. Soc. Chem. Ind.*, 1898, xvii., 1124.

He is unable to confirm the melting points given by Tortelli and Ruggeri; for, working by their method, the highest melting point of the mixture observed was 73·5° C.

Bellier[1] uses more dilute alcohol, and asserts that by his method no mistake is possible when a mixture contains more than 5 or 6 per cent. of earth-nut oil. For a quantitative determination, 5 grammes of the oil are saponified with 25 c.c. of alcoholic potassium hydroxide (85 grammes per litre of 70 per cent.), and the liquid exactly neutralised with acetic acid, and chilled by immersing the vessel in water. After an hour, the precipitate is collected and washed with 70 per cent. alcohol containing 1 per cent. of hydrochloric acid, the temperature being maintained at 15° to 20° C.

The precipitate is dissolved in 25 to 50 c.c. of boiling alcohol (92 to 93 per cent.), from 8 to 16 c.c. of water added to reduce the strength of the alcohol to about 70 per cent., and the liquid again cooled for an hour below 20° C. The precipitate is washed with 70 per cent. alcohol, dried at 100° C., and weighed. A sample of pure Bordeaux earth-nut oil yielded 4·20 per cent. of arachidic acid by this method. Of other oils examined, only one (Tunis olive oil) gave a precipitate corresponding with as much as 1·5 per cent. of earth-nut oil. Other specimens of olive oil gave amounts corresponding with 0·24 to 0·95 per cent.; cotton-seed oil with 0·72 per cent.; and sesamé oil with 0·48 per cent. of earth-nut oil. In the case of numerous French and Spanish oils, the solution remained absolutely clear.

The butter of cows fed upon earth-nut cake does not give any deposit in Renard's test (*Werenskiold*).[2]

The present reviser has made a number of experiments[3] on the solubility of the mixed acids (m.p. 72·5° C.) from a specimen of earth-nut oil, in 90 per cent. alcohol (by volume), in ether and in petroleum spirit. In each case from 2 to 3 grammes of the mixture were dissolved in 200 c.c. to 500 c.c. of the solvent, and the flask immersed in a mixture of ice and water for twelve hours. The solubility at other temperatures was also determined, 10 c.c. of the clear filtrate being evaporated in each case. The results are shown in the following table:—

Solubility of Mixed Lignoceric and Arachidic Acids.

Solvent.	Temperature.	Grammes Dissolved.
100 c.c. of	° C.	
Alcohol, sp. gr. 0·8343 (= 89·9 per cent. by vol.),	0	0·03-0·045
,, ,, (,,),	20	0·175
Petroleum spirit, ...	0	0·040
,, ,, ...	13	0·061
Ether, ...	0	0·42-0·435

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[1] *Ann. de Chim. anal.*, 1899, iv., 4. [2] *J. Soc. Chem. Ind.*, 1899, xviii., 162.
[3] Unpublished.

Hehner and *Mitchell* suggested that their method of determining stearic acid[1] might be applied to the determination of arachidic acid in earth-nut oil, and the results given in the above table show that either petroleum spirit or alcohol would be suitable solvents. Preliminary experiments made by *Hehner* and *Mitchell* in this direction have given promising results.

Jean[2] asserts that he is unable to detect less than 30 per cent. of earth-nut oil in a mixture by Renard's process, and recommends instead the following method, which is essentially a modification of that devised by *Hehner* and *Mitchell*.[3] Ten grammes of the oil are saponified, and the soap dried and treated with 100 c.c. of alcohol (36°) previously saturated with potassium arachidate at 11° to 12° C. The flask is warmed under a reflux condenser until the soap just dissolves, and is then left for twelve hours at a temperature of 15° C. The precipitate is collected, re-crystallised from saturated alcohol, and boiled with 50 c.c. of water containing some hydrochloric acid, in order to liberate the arachidic acid, which is subsequently extracted with petroleum spirit, dried at 100° C., and weighed. Its melting point should not be less than 72° C. The amount of earth-nut oil in the mixture is then calculated on the assumption that edible earth-nut oil contains on the average 4·55 per cent. of arachidic acid.

As a rapid means of detecting a small amount of earth-nut oil in olive oil, *Biazzo* and *Vigdocrik*[4] recommend the following modification of a method suggested by *Kreis* and *Roth*.[5] The solid fatty acids are separated by the lead-ether method, and dissolved in 50 c.c. of 90 per cent. alcohol (containing 10 drops of N-hydrochloric acid per litre), and the flask immersed for 30 minutes in water at 15° C. The crystals which separate are dissolved in 25 c.c. of the alcohol, and the solution again cooled, and if a fresh crop of crystals is obtained they are separated as before, dissolved in 12·5 c.c. of alcohol, the solution cooled once more, and any further crystals dissolved in 5 c.c. of alcohol, which is then allowed to stand at the ordinary temperature. In this way an olive oil containing 5 per cent. of earth-nut oil will yield a sufficient quantity of crystals for determining the melting point, which will be about 73·5° to 74° C.

To obviate errors due to the solubility of arachidic acid in 70 per cent. alcohol, *Evers*[6] has devised the following modification of *Renard's* process:—Five grms. of the oil are saponified for 5 minutes, beneath a reflux condenser, with 25 c.c. of alcoholic potassium hydroxide (80 grms. of KOH in 80 c.c. of water, diluted to a litre with 90 per

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[1] *Analyst*, 1896, xxi., 330.
[2] *Rev. de chim. Ind.*, 1898, ix., 162.
[3] *Analyst* (*loc. cit.*).
[4] *Annali Chim. Applic.*, 1916, vi., 179.
[5] *Zeit. Unters. Nahr. Genussm.*, 1913, xxv., 81.
[6] *Analyst*, 1912, xxxvii., 487, 537.

cent. alcohol). The hot soap solution is treated with 7·5 c.c. of dilute acetic acid (1 : 2) and 100 c.c. of 70 per cent. alcohol containing 1 per cent. (by vol.) of hydrochloric acid. After cooling for an hour at 12° to 14° C., the liquid is filtered, and the residue washed with the mixture of acid and dilute alcohol, until the washings no longer give a turbidity on the addition of water. The residue is dissolved in 90 per cent. alcohol (25 to 70 c.c.) and cooled to a definite temperature between 15° and 20° C. Any crystals are collected after 1 to 3 hours, and washed with 90 per cent. alcohol, and subsequently with 50 c.c. of 70 per cent. alcohol, and then dissolved off the filter by means of ether. The solution is evaporated, and the residue dried at 100° C., and weighed. The crystals should melt above 71° C.; otherwise they should be recrystallised from 90 per cent. alcohol. If only a small quantity of crystals (or none) is produced, sufficient water is added to reduce the strength of the alcohol to 70 per cent., and any crystals separating are washed with 70 per cent. alcohol, weighed, and recrystallised if melting below 71° C.

The following corrections for the solubility of the acid in 90 per cent. and 70 per cent. alcohol are made :—

Weight of Acids Corrected for 90 per cent. Alcohol.	Correction for 100 c.c., 70 per cent. Alcohol.		
	M. Pt. 71° C.	M. Pt. 72° C.	M. Pt. 73° C.
	Grm.	Grm.	Grm.
Above 0·1 grm., ...	0·013	0·008	0·006
0·08 to 0·1 grm., ...	0·011	0·007	0·005
0·05 to 0·08 grm., ...	0·009	0·007	0·005
0·02 to 0·05 grm., ...	0·007	0·006	0·005
Less than 0·07 grm., ...	0·006	0·005	0·004
Factor for converting per cent. fatty acids into earth-nut oil, ...	17	20	22

Adulterants of Earth-nut Oil.—Among the oils which are known to have been used to adulterate earth-nut oil are cotton-seed, sesamé, rape-seed, fish, and mineral oils.

Ponzio[1] has shown that rape-seed oil yields about 0·4 per cent. of "arachidic" acid; but the saponification value and melting point of the fatty acids will furnish evidence of the admixture.

Hydrogenation does not interfere with the detection of arachidic acid.

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[1] *J. prakt. Chem.*, 1893, xlviii., 487.

HAZEL-NUT OIL.

Recorded Values.

Hazel-Nut Oil.

Specific Gravity.	Hehner Value.	Saponification Value.	Iodine Value.	Reichert Value.	Acetyl Value.	Refractive Index.	Authority.
At 15° C.							
0·9169	95·6	193·7	90·2	0·99	3·2	...	Hanus.[1]
0·9115-0·917	...	193-197	86·5-88·5	...	...	...	De Negri and Fabris.[2]
0·9243	...	...	...	...	...	...	Schädler.
0·9158	...	..	82·74	...	...	1·4686	Merrill.[3]
...	...	191·4	83·2	...	...	...	Soltsien.
0·916	95·5	187	87	0·99	...	...	Schoettler.

Fatty Acids.

Melting Point.	Solidification Point.	Saponification Value.	Iodine Value.	Iodine Value of Unsaturated Acids.	Authority.
° C.	° C.				
...	...	200·6	90·6	91·3	Hanus.
22-25	...	...	90·1	...	De Negri and Fabris.
...	19-20	...	...	...	Schoettler.

This oil is obtained from hazel-nuts (*Corylus avellana*), the yield being about 50 to 55 per cent. The cold-drawn oil has a limited use in perfumery, and, owing to its high price, is liable to be adulterated with olive oil. The oil obtained by hot expression is used for burning, soap-making, and lubrication.

It is a mobile yellow liquid, with a characteristic odour recalling that of the nuts.

According to the results obtained by *Hanus* hazel-nut oil consists of 85 per cent. of oleic acid, 10 per cent. of palmitic and stearic acids, 10·4 per cent. of glycerol, and 0·5 per cent. of phytosterol. Neither linolic nor linolenic acid was detected by *Hanus* by the oxidation or bromination methods. The stearic acid amounted to about 1 per cent. No arachidic acid was detected.

In the elaidin test it yields a green semi-solid mass, and this reaction is recommended by *Hanus* for its identification in the presence of olive or almond oils, which have similar iodine values. The iodine value of the "liquid" fatty acids will also afford useful information.

De Negri and *Fabris* state that *Hauchecorne's reaction* (6 grammes of oil heated with 2 grammes of nitric acid, consisting of three parts of acid of 40° B. with one of water, and the colour noted after two and

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[1] *Zeit. Untersuch. Nahr. Genussm.*, 1899, ii., 617.

[2] *Zeit. anal. Chem.*, 1894, xxxiii., 558.

[3] *Maine Agric. Exper. Stat. Bull.*, 1900, [65], 111.

after twenty minutes) will detect 15 per cent. of hazel-nut oil in olive oil, a rose coloration being produced.

Hazel-nut oil solidifies at − 17° to − 20° C., a characteristic that distinguishes it from olive oil.

In the Maumené test *De Negri* and *Fabris* obtained a rise of temperature of 35° to 38° C., whilst *Girard* obtained a similar result.

According to *Merrill* (*loc. cit.*) it produces 9,510 calories per gramme on combustion.

HYOSCYAMUS-SEED OIL.

This oil is contained in the seeds of *Hyoscyamus niger*, from which it can be extracted by suitable solvents.

It is of a pale greenish-yellow colour, and is soluble in 56 parts of absolute alcohol.

A specimen prepared by *Mjoen*[1] had a specific gravity of 0·939 at 15° C., and on saponification yielded oleic, palmitic, and a third unidentified acid.

Oil extracted by *Schwanert*[2] with hot alcohol had a specific gravity of 0·9291.

OLIVE OIL.

HUILE D' OLIVE. OLIVENOEL.

Recorded Values.

Olive Oil.

Origin.	Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Hehner Value.	Reichert-Meissl Value.	Refractive Index.	Authority.
Italian (213 samples),	0·916-0·918	185-196	79·5-88	..	..	..	De Negri and Fabris.
„ (106 „),	..	190-195	79·0-83·2	..	..	..	Oliveri.
Tunisian,	0·917-0·919 (at 15·5° C.)	..	79-88	94·6	..	..	Milliau, Bertainçhand, and Malet.
Californian (11 samples),	0·9162-0·9174	190·5-193·5	80·4-86·5	..	..	..	Blasdale.
..	..	191-193	82-83	..	..	..	Schädler.
Californian,	..	..	77·3-88·7	94-95·9	..	..	Lengfeld and Paparelli.
„	0·9175-0·9180	195	88	..	..	..	Moerk.
..	0·914-0·917	196-206	79-88	..	..	..	Allen.
Dalmatian, .	0·915-0·917	187-195·8	80·7-91·5	..	..	..	Guozdenovic.[3]
Indian, . .	0·9203 (at 15·5 °C.)	190·9	93·67	95·14	0·60	1·4635	Crossley and Le Sueur.
Persian, .	0·9199	190·8	85	..	..	..	Shukoff.
Crimean, .	0·918	186	82·8	..	..	..	„
Tunisian, .	0·9162-0·9175	189·2-191·7	82·7-91·1	..	..	..	Archbutt.
Algerian, .	0·9167-0·9178	190·3-191·7	82·4-90·5	..	..	..	„

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[1] *J. Soc. Chem. Ind.*, 1897, xvi., 340.

[2] *Ibid.*, 1895, xiv., 382.

[3] *Zeit. anal. Chem.*, 1901, xl., 430.

Fatty Acids.

Origin.	Specific Gravity.	Melting Point.	Solidification Point.	Mean Molecular Equivalent	Authority.
		°C.			
Italian (213), .	...	24-27 25-29	...	...	De Negri and Fabris.
,, (106), .	...	...	...	...	Oliveri.
Tunisian, . .	...	34-37	28·8-30·5	...	Milliau, Bertainchand, and Malet.
Californian, .	..	21-26	...	...	Blasdale.
...	...	26·5-28	21·5-22	...	Schädler.
Californian, .	...	28-30	..	...	Lengfeld and Paparelli.
,, .	...	21 (aver.)	...	...	Moerk.
...	0·8430 at 99° C. (Water at 15·5° = 1)	26	21	279·4	Allen.
			Dalican's Test.		
Russian, . .	...	...	21·8	...	Shukoff
Commercial (6),	...	...	18·4-22·9	...	Lewkowitsch.
Californian, .	...	...	25·2-26·4	...	,,

Source.—Olive oil is obtained from the fruit of different varieties of olives, but considering the wide range of country over which the olive is grown for the purpose of oil production, and the number of varieties that have been induced by centuries of cultivation in different climates and on different soils of the different species of *Olea*, it shows much less variation than might *a priori* be expected. Thus *O. europæa* (var. *sylvestris*) was alluded to by Dioscorides as a thorny tree growing wild ('Ελαια ἀγρια); but losing its thorns by cultivation (like the sloe bush, the parent of the garden plums), giving the variety *O. europæa* (var. *sativa*) or 'Ελαια ἡμερα; which again has been the parent of numerous distinct kinds of olive trees producing fruit of very different sizes; thus the so-called "French" olive of the present day is much smaller than the "Spanish" olive.

Apart, however, from these subspecies of *O. europæa* grown in Greece, Phœnicia, Palestine, and the south of Europe since the commencement of the historic period, and thence introduced and acclimatised into such parts of America, Australia, and elsewhere as possess suitable soils and climates, other oil-bearing species are utilised in other countries—*e.g.*, *O. ferruginea* (*O. cuspidata*) in Afghanistan and other Himalayan regions, and *O. capensis* at the Cape of Good Hope.

Causes of Variation.—Even with the best known southern European varieties, notable differences in the quality of the oil extracted are found to exist according to circumstances, more especially according as the fruit has thoroughly ripened on the trees, or has been plucked before it is quite ripe and stored; and according as the oil has been extracted by gentle pressure in the cold, or by hot pressure, especially when accompanied by grinding processes whereby the stones are also broken up and expressed: indeed the differences in quality due to these causes appear to be quite as strongly marked as those due to soil, climate, and degree of cultivation.

The maturity of the olive has a distinct influence on the flavour of the oil, and in the case of Tunisian oil it has been shown that the green fruit yields a product which keeps well, but has a bitter taste; that the oil from black olives is sweeter, but does not keep well; and that the best is obtained from violet olives.[1]

Extraction.—The finest qualities of all are obtained by hand-picking olives from the trees, selecting those not over ripe, but ripe enough to allow oil to exude slightly on gentle pressure between the finger and thumb, and pressing these very gently by hand in cloths. The *virgin oil* thus produced is subsequently agitated with water, and allowed to stand so as to remove mucilaginous matter, the purified oil being skimmed off.

A slightly inferior, but still fine, grade of oil is obtained by crushing ripe olives (preferably with edgestones, but without breaking up the olive kernels), and then pressing cold with comparatively little pressure. The residual marc (known in Italy as *Sanza* or *Nocciulo*) is broken up, stirred with boiling water, and then pressed again with somewhat stronger pressure; the second marc (*Buccia*) is then ground again with heavier millstones so as to crush the olive stones (if this were not done at the first crushing), and is then again stirred up with boiling water and subjected to the heaviest pressure attainable with the appliances used: in small mills these are usually rough screw presses, but in larger ones hydraulic presses are employed. Finally, the residual oil (several per cents.) is extracted from the marc by means of carbon bisulphide or other solvents.

The details of the processes used for extracting olive oil vary widely in different districts and countries. Thus in some establishments the stones are separated from the pericarp and the two treated separately. A superior oil is thus obtained from the pulp, whilst "olive-kernel oil" is extracted from the stones by grinding them to a coarse meal and then pressing or treating with carbon bisulphide, etc. Excepting in being darker coloured and having a more unpleasant odour, the oil thus obtained is said not to differ materially from the lower grade oils obtained from the fruit pulp; it often contains a large percentage of free fatty acids, rendering it more readily soluble in alcohol than ordinary olive oil, thus resembling the "huiles tournantes" derived from the pulp (*infra*).

It has been shown by *Klein*[2] that the freshly-expressed kernel oil differs but little from the fruit oil, and that the high percentage of free acids is due to decomposition before the extraction.

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[1] Milliau, Bertainçhand. and Malet, *Mon. Scient.*, 1900, lvi., 508.

[2] *Zeit. angew. Chem.*, 1898, 847-850.

This is confirmed by *Milliau* and his collaborators,[1] who state, however, that the flavour of pulp oil is preferred by experts to that of the mixed oil from the entire fruit, and that the former fetches a higher price in the market.

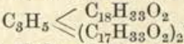
Further particulars of olive-kernel oil are given below.

Qualities of Oil.—In this way several qualities of olive oil are ultimately obtained, more especially *virgin* and *salad* oils of finest flavour, generally greenish through presence of chlorophyll, and of specific gravity near to 0·916 at 15° C.; *huiles d'enfer*[2] or somewhat lower grades of inferior flavour (sometimes with more or less marked acrid after-taste and disagreeable odour); *pyrene* and *sulphocarbon* oils (the former obtained by hot pressing and the latter extracted by carbon bisulphide or other solvent), generally unfit for edible purposes, brownish-yellow, and of specific gravity 0·920 to 0·925 at 15° C.; and "huiles tournantes" obtained from more or less fermented stored fruit, and in consequence considerably rancid, and containing large amounts (25 to 30 per cent.) of free fatty acids. The denser varieties deposit solid matter (mostly palmitin) on chilling somewhat sooner than the lighter ones.

Composition.—Olive oil usually consists of one-fourth glycerides of solid saturated acids (palmitic, etc.), and three-fourths liquid glycerides, mostly olein. This composition would correspond with an iodine absorption of about 67; the somewhat higher values usually found consequently suggest the presence of a small amount of linolic acid. In confirmation of this, *Hazura* and *Grüssner* obtained small quantities of sativic acid (pp. 51, 160) from the products of oxidation of the fatty acids of olive oil, and, judging by the relative quantities of sativic and dihydroxystearic acid, they concluded that the unsaturated acids consisted of about 7 per cent. of linolic acid and 93 per cent. of oleic acid.[3]

Hehner and *Mitchell* did not detect any stearic acid in a specimen of olive oil examined by their method.

The ultimate composition of olive oil, according to *Schädler*, is:—C, 77·20; H, 11·30; and O, 11·50 per cent.

Holde and *Stange*[4] found that olive oil contains from 1 to 2 per cent. of a mixed glyceride, which, from its chemical characteristics, they regarded as oleodimargarin,  $C_3H_5 \begin{smallmatrix} \diagup C_{18}H_{33}O_2 \\ \diagdown (C_{17}H_{33}O_2)_2 \end{smallmatrix}$. This glyceride was isolated by exposing an ethereal solution of the oil to a temperature of − 40° to − 45° C. It showed the following constants:—Saponification value, 196·6; mol. equivalent, 857 to 859·6; iodine value, 29·8 to 30·1; fatty acids, 95·82 per cent.; and specific gravity, 0·9948. On saponification it yielded fatty acids corresponding with the theoretical values of margaric and oleic acids, but subsequent examination (p. 25) showed that the supposed margaric acid was a mixture.

Properties and Tests of Purity—*Spectrum.*—Olive oil shows a deep band in the blue, violet, and in the red, with faint lines in the green and orange parts of the spectrum. Refined cotton-seed oil shows

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[1] Milliau, Bertainchand, and Malet, *Mon. Scient.*, 1900, lvi., 508.

[2] So-called because the oil (mixed with water to separate mucilage by standing) is stored in large underground tanks or reservoirs so as to avoid exposure to air as much as possible.

[3] *Monatsh. f. Chem.*, 1889, ix., 944-6.

[4] *Ber. d. d. chem. Ges.*, 1901, xxxiv., 2402.

the same band in the blue and violet, but in the green and red the spectrum is continuous.

Electrical Conductivity.—*Rousseau* states that olive oil has 675 times less conductivity than other oils, and that the least addition of these increases the conductivity as observed by means of his *diagometer* (*q.v.*).

Action of Heat.—When heated to 120° C. olive oil becomes lighter in colour. At 220° C. it becomes nearly colourless, and at the same time rancid. At 315° C. it is decomposed (*Allen*).

Specific Gravity.—The specific gravity varies considerably with the method of extraction, and is highest when the oil is expressed at a higher temperature, and thus contains a larger amount of the glycerides of solid fatty acids.

Admixture with heavier oils, such as cotton-seed oil, tends to raise the specific gravity; whilst, conversely, addition of rape oil tends to lower it; thus, *Souchère* [1] gives the following table indicating the effect of such admixtures on the relative density at 15° C. of pure olive oil.

Oil.	Specific Gravity at 15° of Pure Oil.	Percentage Added.				
		10	20	30	40	50
Olive,	0·9153	...	...	...	...	...
Colza,	0·9142	0·91519	0·91508	0·91497	0·91486	0·91475
Sesamé,	0·9225	0·91602	0·91674	0·91741	0·91818	0·91890
Cotton-seed,	0·923	0·91607	0·91684	0·91761	0·91838	0·91915
Arachis,	0·917	0·91547	0·91564	0·91581	0·91598	0·91615

These results were obtained by means of Lefebre's oleometer (*q.v.*). Although the specific gravity may indicate adulteration with cotton-seed oil or sesamé oil, it is obviously of no value for the detection of rape or earth-nut oils.

Refractive Index.—This was found to vary from 0° to + 2° by *Oliveri*,[2] who examined 106 specimens of olive oil and a number of other oils in Jean's oleo-refractometer, with the following results:—

Oil.	Oleo-Refractometer Reading.
Olive (106 samples),	0-2°
Cotton-seed,	18
Sesamé,	15·5
Colza,	26·5
Earth-nut,	7·5
Poppy,	28·5
Castor,	41·4

With the exception of earth-nut oil, any considerable addition of these oils will be indicated by an increased refractometer reading.

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[1] *Mon. Scient.*, xi., 791.

[2] *Staz. Sper. Agrar. Ital.*, xxiv., 387.

Procter gives the refractive index of olive oil (mean of 4) at 1·4715 at 15° C., and 1·4546 at 60° C. With a sample of Indian oil, *Crossley* and *Le Sueur* observed a refractive index of 1·4635 in a Zeiss refractometer.

Solidifying Point.—Olive oil becomes turbid at + 2° C. and at – 6° C. deposits about 28 per cent. of solid substance, whilst cotton-seed oil becomes turbid at about 12° C. and solid at 0° C. to – 1° C. When cooled to – 20° C. it yields a remarkably hard mass, and a test for the presence of cotton-seed oil has been based upon this fact by *S. Carpi.*[1]

The oil is cooled to – 20° C. for three hours, and the hardness of the product obtained tested by means of a cylindrical iron cone, 1 cm. long and 2 mm. in diameter, on the base of which weights are placed until it penetrates the mass. *Carpi* found that the best olive oil required 1,750 grammes, whilst poorer qualities invariably required more than 1,000 grammes. For cotton-seed oil only 25 grammes were necessary, whilst for mixtures intermediate values were obtained.

A somewhat analogous test has been devised by *Goldberg,*[2] in which the time and temperature at which the solidified mass becomes liquid again are noted. Thus, pure olive oil cooled for two and three-fourth hours at – 15° to – 20° C. began to melt in 55 minutes, and was completely liquid after 185 minutes, the temperature then being + 11·5° C. A mixture of 95 per cent. of olive oil and 5 per cent. of cotton-seed oil began to melt after 50 minutes, and was completely fluid after 162 minutes (temperature, + 12·5° C.).

It was found [3] that pure old olive oil required longer time to melt than fresh oil, and that the time was reduced by bleaching and by exposure to light.

Melting and Solidifying Points of the Fatty Acids.—In many cases evidence of adulteration is obtainable by saponifying the oil, separating the fatty acids, and determining their melting and solidifying points *side by side with the corresponding acids obtained from genuine oil, or mixtures of known composition,* as the precise numbers obtained vary according to the particular mode of manipulation adopted. Values varying from 22° to 29° C. for the melting point, and from 21° to 25° C. as the solidifying point, have been recorded by different observers. Tunisian oils have given much higher figures, whilst the fatty acids from Californian oils sometimes melt at as low as 19° C. (see *Table of Constants*).

Dieterich gives the following comparative values, using the same process throughout :—

	Melting Point.	Solidification Point.
Olive oil (average of 19 samples), . .	26° to 28·5°	23·4° to 24·6°
3 parts olive oil to 1 of earth-nut oil, .	29	26
,, ,, cotton-seed oil, .	30	27·3
,, ,, sunflower seed oil,	25	20·5
,, ,, sesamé oil, . .	28	25
,, ,, linseed oil, . .	24·5	19·5
,, ,, colza oil, . .	23·0	19

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[1] *Annali Chim. applic. ; Zeit. anal. Chem.*, xxiii., 566.

[2] *Chem. Zeit.*, 1897, xxi., 304.

[3] *Chem. Zeit.*, 1898, xxii., 991

A similar series of results is given by *Bach*.[1]

The figures thus deduced, however, are not sufficiently decisive of themselves to warrant any accurate deduction being drawn as to the nature and extent of the adulteration.

The solidifying point by Dalican's method was found by *Lewkowitsch* to vary in twelve samples from 16·9 to 26·4.

Cohesion Figure.—Examination of the cohesion figure formed when oil is placed on water, has been recommended by *Tomlinson* as a useful test of the purity of olive oil. A drop of oil is allowed to fall gently on the surface of pure water contained in a chemically clean basin of sufficiently large size, at a temperature not below 15° C. In the case of pure olive oil the drop slowly spreads out into the shape of a large disc with slightly recurved edges; little spaces shortly appear round the edge, the film commencing to retract again, so that the edge resembles a string of beads. The spaces between the beads soon open out more, and the edge becomes toothed; portions become detached, re-uniting themselves in some places to the main oil film enclosing polygonal spaces bounded by fine beads, and covered by a dew of oil so fine as to be visible only with difficulty. About 35 seconds are required for the entire succession of changes.

With sesamé oil the film first formed soon begins to contract again, ultimately forming a figure consisting of a central spot with distinctly marked rays, between which other smaller rayed spots appear, the whole resembling a spider's web loaded with dew; about 60 seconds are required to complete these changes.

Mixtures of olive and sesamé oils give figures of intermediate character, the features of the one or the other figure predominating according as the first or the second oil forms the majority of the mixture; and analogous differences in the olive oil figure are produced by admixture with other oils.

Free Fatty Acids.—The acidity of the oil from hand-picked olives expressed with as little delay as possible is about 0·3 per cent., as oleic acid; usually it is much higher ranging from about 1·0, and 8·33 has been recorded in one instance.[2] It is possible, however, that the olives were allowed to lie some time before expression, which has been shown to increase the acidity.

Filtration of the oil has a great influence in preventing the development of further acidity. Thus *Milliau*, *Bertainçhand*, and *Malet*[3] found that the acidity of unfiltered oil increased in two months from 0·3 to 0·7 per cent., whereas the same oil, after filtration, did not alter in that time.

Archbutt[4] determined the acidity (as oleic acid) of olive oils from various sources, with the subjoined results. All the samples were intended for lubricating purposes:—

Origin.	Number of Specimens.	Acidity as Oleic Acid.		
		Maximum.	Minimum.	Mean.
		Per cent.	Per cent.	Per cent.
Spain, . . .	70	25·1	1·5	5·5
Italy, . . .	36	25·2	0·9	8·5
Sicily, . . .	28	16·6	0·5	9·1

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[1] *Zeit. anal. Chem.*, 1884, xxiii., 259.

[2] Californian oils. Moerk, *loc. cit.*

[3] *Loc. cit.*

[4] *J. Soc. Chem. Ind.*, 1889, viii., 685.

Reichert Value.—In the oil freshly extracted from sound olives this is very low, only amounting to 0·3 or 0·4. With the increase of the free fatty acids there is also an increase in the amount of volatile acids.

Hence *Scala* [1] employs this figure as a measure of the rancidity of an oil, determining the Reichert-Wollny value on 5 grammes. He suggests the limit of 2 c.c. of decinormal alkali for edible olive oil.

Crossley and *Le Sueur* obtained the value 0·6 with a specimen of Indian oil.

Iodine Value.—This is usually about 83, although in Californian and Tunisian oils it often rises as high as 88; and *Crossley* and *Le Sueur* give the unusual figure 93·67 for a specimen of Indian oil. According to *Lengfeld* and *Paparelli* [2] it varies from 79 to 88, the variations depending on the maturity of the olives and age of the oil. The method of extraction has also an influence, oils extracted by solvents having a lower value than those obtained by expression.

Goldberg [3] has shown that there is practically no difference between the iodine value of the semi-solid mass which is deposited on chilling the oil and that of the more liquid portion.

Any admixture with poppy-seed oil, and to a less extent with sesamé, cotton-seed, and rape oils, distinctly increases the iodine number.

The heat of bromination was shown by *Hehner* and *Mitchell* to be proportional to the iodine value, and this has been confirmed by *Archbutt*,[4] who made comparative determinations with ten specimens of olive oil.

Saponification Value.—This has been found by different observers to vary from 185 to 206 (*Allen*). The better grades, however, yield a value of about 190. Any considerable addition of rape oil (saponification value about 175) would lower this figure materially.

Allen found the mean molecular equivalent of the free fatty acids to be 279·4.

The Elaidin Test serves to distinguish adulteration with many oils giving soft elaidins; a distinct softening of the product as compared with that obtained with pure oil treated side by side is noticeable when only a small percentage of poppy-seed or linseed oil are present, and with somewhat larger proportions of cotton-seed, rape-seed, or sesamé oils.

Moreover, the elaidin formed with pure olive oil is nearly colourless or pale yellow, whereas much darker tints are generally produced by adulterated oils. On this property numerous modifications of the nitric acid test have been proposed by various observers for the purpose of examining olive oil.

With Californian oils *Blasdale* obtained a reaction within thirty minutes to six hours.

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[1] *Analyst*, 1896, xxi., 298.

[2] *J. Soc. Chem. Ind.*, 1892, xi., 848.

[3] *Chem. Zeit.*, 1897, xxi., 304; *J. Soc. Chem. Ind.*, 1897, xvi., 448.

[4] *J. Soc. Chem. Ind.*, 1897, xvi., 311.

Archbutt[1] has published a series of tables to illustrate the effect on the elaidin reaction of adding nut, rape, or cotton-seed oil to olive oil, and from these the following particulars may be quoted :—

Oil.	Minutes for Solidification at 25° C.	After 24 Hours at 25° C.	
		Colour.	Consistence.
Olive, ...	230	Lemon yellow	Hard but penetrable.
,, + 10 per cent. best nut,	300		Softer than pure olive.
,, + 10 ,, rape, .	320	Pale orange	Buttery.
,, + 20 ,, ,, .	9-11½ hours	Deeper orange	
,, + 10 ,, cotton,	9-11½ ,,	Lemon yellow	Very soft butter.
,, + 20 ,, ,, .	More than 11½ hours		

The Maumené Test.—The following table gives some of the various results that have been obtained by different observers, each of whom make the determination under different conditions :—

Authority.	Method.	Rise.
		° C.
Maumené, ...	50 grammes oil ; 10 c.c. H_2SO_4 (66° Bé.). Beaker, ...	42
Archbutt, ...	50 grammes oil ; 10 c.c. H_2SO_4 ($97^{\circ}/_{\circ}$). 7-oz. beaker packed in wool, . .	41-45
Lengfeld and Paparelli, .	... ...	33·5-41
Jean, ...	Thermelæometer, ...	41·5
De Negri and Fabris, .	,, ...	32-37
Blasdale, ...	15 c.c. of oil ; 5 c.c. H_2SO_4, ...	45-47
Thomson and Ballantyne,	Beaker. H_2SO_4, 97 per cent., .	41·4
,, ,, ,,	Specific temperature reaction, . .	89-95
Mitchell, . . .	Halogen standard figure. (H_2SO_4. 97·8%),	18·4

Mitchell[2] has shown that the "Halogen standard Maumené figure" is proportional to the iodine value, as indeed had been asserted by *Lengfeld* and *Paparelli* with reference to their cruder method of determining the rise of temperature.

Solubility in different Liquids.—Olive oil dissolves in alcohol to the extent of 0·38 per cent. whilst 3 parts are soluble in 5 parts of ether. Valenta's test (*q.v.*) may sometimes afford corroborative evidence of purity, especially when made side by side with genuine oil and mixtures of known composition.

Extracted Olive Oil.—The characters of olive oils extracted with carbon bisulphide differ considerably from those of expressed oils.

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[1] *J. Soc. Chem. Ind.*, 1886, v., 308.

[2] *Analyst*, 1901, xxvi., 169.

They have a higher specific gravity (0·920, Fritsch; 0·927, Klein, at 15·5° C.), a lower iodine value (77·5 to 80·2), and a lower refractometer reading (59° to 61°, Zeiss), except in the case of oils which have been bleached by oxidation, the refractometer reading of which is higher (63°). Their fatty acids also show a lower melting point than the normal figure (17·5° to 19·7° C.).

As a test for the sulphur in these oils, *Canzoneri* and *Bianchini*[1] shake 10 c.c. of the oil with a globule of mercury, and allow the tube to stand for some time, or heat it for 15 minutes at 100° C. Mercaptans, which are invariably present in commercial extracted oils, may be detected by distilling the sample in a current of steam and testing the distillate with mercuric chloride.

Or carbon disulphide may be detected by *Milliau's*[2] method, in which 50 grms. of the oil are distilled with 10 c.c. of amyl alcohol, and 4 c.c. of the first 5 c.c. of the distillate is mixed with 1 c.c. of kapok or cotton-seed oil and a trace of sulphur, and heated for an hour in a sealed tube.

In recent methods of refining, industrial oils are heated at 38° to 45° C., and steamed at a low temperature to remove sulphur compounds of unpleasant odour. Colza and ravison rape oils do not show the mercury reaction, and only contain traces of sulphur, especially when refined. They may be distinguished, however, from extracted olive oils by their high refractometer reading (70°).

Archbutt,[3] who has examined a large number of Algerian and Tunisian olive oils of undoubted purity, found them to contain not more than traces of arachidic and lignoceric acids.

Olive-residuum Oils.—In poor seasons, when genuine oil is scarce, the marc or pulp left in the press is worked up for lubricating purposes as described above. After neutralising the free fatty acids with alkali and washing out the soap, such oils are put upon the market as "neutral" or "saponified" oils, and are usually sold with a guarantee that the acidity does not exceed a definite amount (1 to 4 per cent.).

Commercial samples of such oils examined by *Archbutt*[4] had the following characters:—Sp. gr., 0·9165-0·9175; free oleic acid, 0·9 to 2·9 per cent.; saponification value, 185·4-186·9; iodine value, 84·4-86·5; and unsaponifiable matter, 2·34 to 3·32 per cent. None of the nine samples yielded any arachidic acid in Renard's test.

Colour Reactions.—Numerous tests have been based upon colours given by different oils with various reagents and not by olive oil; but only the following have as yet established their claim:—

Becchi's Test for cotton-seed oil gives useful indications of the presence of that adulterant, provided that the refining of the cotton-seed oil has not been carried so far as to bring about the entire withdrawal of the constituent that acts on the silver nitrate.

Genuine olive oils which give any discoloration in this test have

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[1] *Annali Chim. Applic.*, 1914, ii., 1. [2] *Ann. Chim. Anal.*, 1912, xvii., 1.

[3] *J. Soc. Chem. Ind.*, 1907, xxvi., 453, 1185.

[4] *Ibid.*, 1911, xxx., 5.

usually been badly refined, and *De Negri* and *Fabris* found that in the few instances in which refined oils gave a slight reaction, this could be prevented by filtering several times.

In the case of Tunisian oils, *Milliau* and his collaborators found that occasionally a brown coloration was given by the oils, but not by their fatty acids.

See also *Nitric Acid Test* and *Halphen's Test*, described under *Cotton-seed Oil.*

Baudouin's Test (see *Sesamé Oil*).—According to *Villavecchi* and *Fabris*,[1] olive oil of undoubted purity from various localities in Italy gives the same red coloration to the aqueous layer as other oil to which 5 per cent. of sesamé oil has been added; but if the agitation be only kept up for one minute, in the case of such pure olive oils, the aqueous layer immediately separates and remains colourless for at least two minutes; whilst the milky oily layer remains greenish or yellowish. If only a minute quantity of sesamé oil be present, however, this oily layer turns red; the coloration of the oil, rather than of the watery fluid, is the distinctive part of the test.

De Negri and *Fabris* obtained negative results with all the expressed oils examined by them, and *Milliau* did not observe the coloration with Tunisian oils.

Milliau, however, has shown that certain olive oils contain a colouring matter derived from the aqueous part of the olive, and that these give a rose coloration with Baudouin's reagent. This can be obviated by testing the dried fatty acids.

Silva[2] has observed the same fact in the case of certain Portuguese oils. He, therefore, prefers Tocher's reagent which gives a negative result with these oils.

According to *Carlinfante*,[3] the red coloration sometimes given by pure oils with Baudouin's reagent may be removed by shaking the acid layer with three times its quantity of water. If only 0·5 per cent. of sesamé oil be present the red coloration is not removed by this treatment.

Detection of Hydrocarbons.—Admixtures of hydrocarbons may be detected by completely saponifying the oil with alcoholic sodium or potassium hydroxide, evaporating off most of the spirit and adding water, shaking up with ether, separating the ethereal liquid and evaporating the solvent. With pure oil only infinitesimal amounts of unsaponified matter (phytosterol, etc.) will be left, whereas hydrocarbon oils, if present, will be obtained in much larger quantity after evaporation of the ether. This test may be made a quantitative one by using a weighed amount of oil and evaporating a known fraction of the ethereal solution in a weighed vessel (*vide* p. 170).

Owing to the scarcity of olive and other vegetable oils, so-called "salad oils," consisting of deodorised paraffin oil coloured with an

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[1] *J. Soc. Chem. Ind.*, 1893, xii., 67.

[2] *Bull. Soc. Chim.*, 1898, xix., 88; *Analyst*, 1898, xxiii., 77.

[3] *Chem. Zeit. Rep.*, 1895, 215; *Analyst*, 1895, xx., 215.

organic dyestuff, were extensively sold during the war. Several convictions for the sale of these products have been obtained under the Food and Drugs Act.

Metals in Olive Oil.—Occasionally metallic compounds are found in solution in olive oil or substances purporting to be such; thus copper (added to communicate a chlorophyll-like green shade) is sometimes present. Lead compounds are said to be occasionally added for the purpose of communicating a sweeter taste to the oil. Metallic impurities of this kind may be detected as described on p. 174.

Detection of other Oils.—Several special instruments have been invented for the purpose of examining olive oil, in order to detect adulterations, based on different physical properties—*e.g.*, the *thermal aræometer*, the *oleorefractometer*, and the *diagometer*. The polariscope may also be utilised, olive oil being slightly dextro-rotatory, and most other oils lævo-rotatory.

Earth-nut Oil.—As a rule, the iodine value of this oil exceeds that of olive oil (see *Constants*). The most important test is the determination of arachidic acid (*q.v.*), which, as a rule, only occurs in traces in olive oil, although certain Tunisian oils give a deposit in the test corresponding with about 1·5 per cent. of earth-nut oil.

Castor Oil.—See *Recorded Values; Solubility in Alcohol.*

Cotton-seed Oil.—This has a higher specific gravity and iodine value than olive oil. The Maumené test and elaidin reaction will afford confirmatory evidence. See also *Halphen's* and *Becchi's phytosterol tests.*

Curcas Oil.—This is stated by *Schädler* to be used to adulterate Portuguese olive oil (see *Values of Curcas Oil*). On treating a mixture of curcas and olive oil with copper and nitric acid the mass is said to acquire a reddish-brown colour after a short time.

Fish Oils and *Drying Oils* have a high iodine value, and yield precipitates with bromine.

Rape Oil.—See *Recorded Values.*

A method of detecting rape oil in olive oil has been based by *Biazzo* and *Vigdorcik*[1] on the hydrogenation of the erucic acid into behenic acid. The fatty acids from 20 grms. of the oil are dissolved in 180 c.c. of anhydrous acetone, and the solution heated to incipient boiling, treated with 20 c.c. of N-potassium hydroxide solution, and cooled at 15° C. The precipitated soaps are separated with the aid of a pump, washed four times with successive portions of 10 c.c. of cold acetone, and dissolved in water, and the solid fatty acids liberated by the addition of hydrochloric acid and 100 c.c. of ether. The ethereal solution is washed twice with 100 c.c. of water, and shaken for 5 minutes with 15 c.c. of a 30 per cent. aqueous solution of lead acetate, and the insoluble lead soaps tested for arachidic and lignoceric acids. The ethereal solution, which will contain the lead salts of the liquid fatty acids and of erucic acid, if rape oil be present, is washed free from

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[1] *Annali Chim. Applic.*, 1916, vi., 185.

mineral acid, and hydrogenated in the presence of finely divided palladium. The ether is distilled and the hydrogenated fatty acids are fractionally crystallised (*vide supra*). If the last fraction melts above 71° C. the presence of behenic acid is indicated. As a rule, in the case of oils containing rape oil, the melting point of the crystals finally obtained is from 76° C. upwards. Hydrogenation of erucic acid in ethereal solution yielded behenic acid melting at 78·5° C., and, after three recrystallisations from alcohol, at 82° C. Behenic acid is also characterised by its sparing solubility in 90 per cent. alcohol.

OLIVE-KERNEL OIL.

Recorded Values.

Olive-Kernel Oil.

Origin.	Specific Gravity.	Iodine Value.	Saponification Value.	Free Fatty Acids.	Refractive Index.	Authority.
				Per cent.		
Commercial, . .	0·9277	71·57	190·5	71·12	...	Klein.
Freshly extracted (Portuguese),	0·9186 to 0·9191	86·99 to 87·78	182·3 to 183·8	1·00 to 1·78	1·4688	,,

This oil has usually been regarded as differing from the fruit oil in its taste, colour, and large proportion of free fatty acids. *Klein*, however, has shown that this is due to the manner of extraction, the mass being left for several weeks after the removal of the pulp oil, so that the oil subsequently expressed has a dark green colour, due to chlorophyll, and a very high percentage of free acids.

If, however, the oil be freshly extracted, it has properties approximating to those of olive oil, though the specific gravity and iodine value are somewhat higher than those of the average oil.

Composition.—*Klein* found the kernel oil to contain 9·7 per cent. of solid fatty acids, consisting of 40 per cent. of stearic acid and 60 per cent. of palmitic acid. The liquid fatty acids, examined by Hazura's method, were found to consist of oleic and linolic acids. No arachidic acid was detected.

Mixed Pulp and Kernel Oil.—*Klein* found that the kernel oil was not so liable to become rancid as had previously been stated. A specimen of oil was kept for seven years in a closed bottle in the dark, and at the end of that time only showed an increase of 0·2 per cent. in its acidity. He therefore came to the conclusion that there was no reason why the fruit and stones should not be crushed together. On this point, however, see p. 484.

The following tables, given by *Milliau*, *Bertainçhand*, and *Malet*, represent the characteristics of the mixed oil from the pulp and kernel and that obtained from the pulp alone :—

Oil.

Tunisian Oil.	Specific Gravity at 15·5° C.	Acidity as Oleic Acid.	Iodine Value.	Solubility in Absolute Alcohol at 15·5° C.
Pulp and kernel—		Per cent.		Parts per 1000.
1st Expression,	0·9190	1·2	83·6	40
2nd ,,	0·9188	1·2	82·6	41
Pulp alone—				
1st Expression,	0·9189	0·8	84·8	40
2nd ,,	0·9191	1·5	88·3	41

Fatty Acids.

Tunisian Oil.	Melting Point.	Solidification Point.	Total Fatty Acids.	Liquid Fatty Acids.	Solid Fatty Acids.
Pulp and kernel—	° C.	° C.	Per cent.	Per cent.	Per cent.
1st Expression,	34·5	29·0	96·02	75·0	25·0
2nd ,,	34·0	28·8	95·15	74·4	25·6
Pulp alone—					
1st Expression,	36·8	29·5	95·35	75·7	24·3
2nd ,,	37·0	30·5	95·35	75·2	24·8

PARADISE-NUT OIL.

Recorded Values.[1]

Paradise-Nut Oil.

Specific gravity,	0·895 at 15° C.
Solidification point,	4° C.
Melting point of fatty acids,	37·6°
Solidification point of fatty acids,	28·5°
Saponification value,	173·63
Iodine value,	71·64
,, fatty acids,	72·33
Acid value (as oleic acid),	3·19
Acetyl value,	44·08
Refractometer (*Zeiss-Wollny*),	61·3-61·5 at 15° C.

This oil is extracted from the kernels of *Lecythis zabucajo*, a tree belonging to the *Myrtaceæ*, growing in the forests of Brazil and Guiana.

De Negri obtained 50 to 51 per cent. of a mobile, clear, light yellow oil by extraction with petroleum spirit. This oil readily became rancid, though less rapidly than Brazil-nut oil. When cooled to 12° C. it began to solidify, and at 4° C. was completely solid.

It dissolved in an equal volume of hot glacial acetic acid, but was insoluble in cold absolute alcohol.

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[1] De Negri, *Chem. Zeit.*, 1898, xxii., 961.

PEACH-KERNEL OIL.

Recorded Values.

Oil.

Specific Gravity.	Acid Value.	Saponification Value.	Iodine Value.	Critical Temp. of Solution.	Butyro-refractometer.	Solidification Point.	Authority.
				° C.			
0·918 at 15° C.,	..	192·5	92·5 to 93·5	..	..	..	De Negri and Fabris.
0·918 to 0·9632 at 15° C.,	5·46 to 6·53	163 to 192·5	92·5 to 109·7	41	67·2 at 25° C. 58·5 at 40° C.	below −20° C.	Dieterich.[1]
0·92147 at 15° C.,	0·52	191·11	99·7	..	52·2 at 50° C.	..	Micko.[2]
0·9198	1·51	191·4	95·2	..	57·5	..	Lewkowitsch.
..	..	..	..	..	Oleo-refractometer. 7·5 to 11·5	..	Pearmain.

Fatty Acids.

Melting Point.	Solidification Point.	Saponification Value.	Iodine Value.	Authority.
° C.	° C.			
...	...	...	94·1	De Negri and Fabris.
3-5	...	...	94·1-102·0	Dieterich.
...	...	200·87	101·93	Micko.
10-18·9 [3]	Dalican's Test. 13-13·5	205·1	...	Lewkowitsch.

This oil, which is expressed or extracted from peach-kernel (*Amygdalus persica*), closely resembles almond oil in appearance and properties, and is largely employed as an adulterant of the latter.

The tests suggested for its detection are described under *Almond Oil.*

PISTACHIO-NUT OIL.

Recorded Values.

Pistachio-Nut Oil.

Specific Gravity.	Saponification Value.	Iodine Value.	Maumené Test.	Heat of Combustion Calories per Gramme.	Refractive Index at 20° C.	Solidification Point.	Authority
			° C.			° C.	
0·9185	191	87	45	...	...	-8 to -10(*a*) -5 to - 8(*b*)	De Negri & Fabris.[4]
0·9134(*b*)	...	83·82	...	9412	1·4687	...	Merrill.[5]

(*a*) Expressed oil. (*b*) Extracted oil.

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[1] *Chem. Rev. Fett Ind.*, 1901, viii., 210.

[2] *Analyst*, 1893, xviii., 149.

[3] Capillary tube method.

[4] *Zeit. anal. Chem.*, 1894, xxxiii., 565.

[5] *Maine Agric. Exper. Stat. Bull.*, 1900, [65], iii.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
°C.	°C.		
17-20	13-14	88·9	De Negri and Fabris.

This oil, which is obtained from the seeds of *Pistacia vera* or *P. lentiscus*, is used in the manufacture of sweetmeats.

When obtained by expression it has a golden yellow colour, whilst the oil extracted by means of ether or petroleum spirit is dark yellowish-green. The green colouring matter, possibly chlorophyll, can be partially removed by treating the oil with alcohol.

On treatment with nitric acid (3 : 1) this oil gives a green coloration, and yields a solid elaidin after twelve hours.

PLUM-KERNEL OIL.

Recorded Values.

Plum-Kernel Oil.

Specific Gravity.	Refractive Index.	Acid Value.	Saponification Value.	Iodine Value.	Maumené Test.	Solidification Point.	Authority.
At 15° C.					°C.	°C.	
0·9195	..	0·55	191·53	100·20	..	..	Micko.[1]
0·916	..	..	191·4	100	44·45	−5 to −6	De Negri & Fabris.[2]
0·9127	..	..	..	..	..	−8·7	Schädler.
0·9193-0·9213	61·5-66·7	..	188·1-198·5	103·6-121·1	..	..	Alpers.

Fatty Acids.

Melting Point.	Solidification Point.	Saponification Value.	Iodine Value.	Mean Molecular Weight.	Authority.
°C.	°C.				
12·4-18	..	200·47	104·21	279·34	Micko.
20-22	13-15	..	102	..	De Negri & Fabris.

Plum-kernel oil is obtained from the kernels of the fruit of the plum tree (*Prunus domestica*, and *P. damascæna*).

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[1] *Analyst*, 1893, xviii., 149.

[2] *Zeit. anal. Chem.*, 1894, xxxiii., 558.

According to *De Negri* and *Fabris*, it is used, especially in Würtemburg, as an edible oil, and for burning.

Utz[1] obtained a yield of 30·15 per cent. of oil from plum stone kernels. This had the normal characteristics of the oils examined by Alpers (*supra*).

It resembles almond oil in its characteristics, and is sometimes used to adulterate that oil.

According to *Micko*, plum-kernel oil gives a yellow coloration, changing to dull orange, with nitric acid of specific gravity 1·4.

With Bieber's reagent ($H_2SO_4 + HNO_3 +$ water) it gives a rose coloration.

RICE OIL.[2]

Recorded Values.

Rice Oil.

Origin.	Free Fatty Acids.	Saponification Value.	Iodine Value.	Melting Point.	Authority.
	Per cent.			° C.	
Expressed from Rangoon meal, . . .	64	193·2	96·4	...	Smetham.
Extracted, . . .	77·2	192·0	99·9	29	,,
Extracted from husk-free meal, . . .	43·4	195·8	96·9	...	,,

According to *Smetham*, common rice contains from 8 to 19 per cent. of oil, whilst Rangoon rice meal contains about 15 per cent.

The oil obtained by expression is semi-solid, and of a dirty green colour. That expressed or extracted from imported grain contains a remarkably high proportion of free fatty acids, but it is not improbable that the perfectly fresh seed would yield a more neutral oil.

The "polishings" obtained in preparing rice for the market were, prior to the war, exported from Italy to Germany and Switzerland, and bought on the combined content of proteins and fat. As a rule, they contain about 6·5 per cent. of crude oil, which frequently has a high acid value owing to enzymic action. A specimen extracted by *Garello*[3] had the following characters:—Melting point, 25°-26° C.; acid value, 90; saponification value, 186; Hehner value, 95·2; iodine value, 99·7; glycerol, 4·95 per cent.; and unsaponifiable matter, 3·2 per cent.

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[1] *Chem. Umschau*, 1919, xxvi., 47.

[2] Smetham, *Analyst*, 1893, xviii., 191.

[3] *Annali Chim. Applic.*, 1917, viii., 109.

STROPHANTHUS-SEED OIL.

Recorded Values.

Strophanthus-Seed Oil.

Specific Gravity.	Acid Value.	Saponification Value.	Hehner Value.	Reichert Value.	Iodine Value.	Melting Point.	Solidification Point.	Authority.
						°C.	°C.	
0·9247 at 21° C. .	...	179·5	92	...	95·6	...	...	Fischer.[1]
0·9254 .	...	187·9	95·3	0·5	73·02	...	...	Mjoen.
0·9249 at 15° C. .	24·3	194·6	94·1	0·9	101·6	2	−6	Bjalobrsheski.[2]

Fatty Acids.

Melting Point, . . .	32·2° C. (Bjalobrsheski).

This oil is contained in the seeds of *Strophanthus hispidus*, which yield about 13 per cent. on expression, and an additional 9 to 10 per cent. on subsequent extraction with ether.

It has a narcotic odour due to the presence of a considerable proportion of essential oil, which can be distilled off in a current of steam, leaving a greenish-red fatty oil. The presence of this essential oil probably explains the marked difference in the values recorded above, those of Bjalobrsheski having been obtained with oil free from essential oil. On exposure to sunlight the oil is bleached, but does not dry.

According to *Bjalobrsheski*, it contains oleic, stearic, and arachidic acid, with traces of formic acid and another volatile acid, and phytosterol.

TEA-SEED OIL.

HUILE DE THÉ. THEESAMENOEL.

Recorded Values.

Oil.

Origin.	Specific Gravity at 15° C.	Hehner Value.	Saponification Value.	Iodine Value.	Solidification Point.	Authority.
					°C.	
Chinese tea,	0·917-0·927	..	..	..	− 5	Schädler.
Assam tea,	0·920	91·5	194	88 .	−12	Itallie.[3]
..	..	..	195·5	..	..	Davies.
..	..	..	190·1	90·49	..	Lane.
Assam, .	0·9208	..	189·9	92·7	..	Menon.
Chinese, .	0·9163	..	..	84·35	..	Bolton & Revis.

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[1] *J. Soc. Chem. Ind.*, 1887, vi., 676.
[2] *Chem. Rev. Fett Ind.*, 1901, viii., 123.
[3] *J. Soc. Chem. Ind.*, 1893, xii., 848.

Tea-seed oil, obtained from the seeds of *Camellia theifera*, is a clear, light yellow liquid, with a more or less pronounced acid taste.

It is expressed in China, where it is used as an edible oil, in the manufacture of soap, and for illuminating purposes. A sample of Assam seeds yielded 16·1 per cent. of oil when extracted with petroleum spirit.[1]

According to the *Indian Tea Association*,[2] however, tea-seed oil cannot be used with safety as an edible oil, owing to the presence of saponin, and there is the same objection to its use as a food for cattle.

Tea-seed oil closely resembles olive oil in its general chemical properties. When subjected to the action of nitrous acid it yields a hard elaidin.

Lane[3] obtained, by treatment of the lead salts with ether, 88 to 93 per cent. of "liquid" fatty acids with an iodine value of 99·6 to 104·4.

According to *Cofman* and *Nicoresti*,[4] olive oil is now largely adulterated with tea-seed oil. It may be detected if present in some quantity by shaking the oil with a mixture of sulphuric and nitric acids and water, and keeping the tube for twenty minutes in boiling water. The oil layer becomes pink if tea-seed oil or a mixture containing 20 per cent. of that oil is present.

UNGNADIA OIL.[5]

Recorded Values.

Ungnadia Oil.

Specific gravity at 15° C.,	0·9120
,, ,, 100° C.,	0·854
Solidification point,	– 12° C.
Saponification value,	191-192
Hehner value,	94·12
Iodine value,	81·5-82
,, of fatty acids,	86-87
Melting point ,,	19° C.
Solidification point ,,	10° C.

This oil is obtained from the fruit of the plant *Ungnadia speciosa*, which is indigenous to Texas, but is now also found in Mexico and other parts of North America.

The seeds contain from 40 to 50 per cent. of a pale yellow oil, which

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[1] Menon, *Year Book Ind. Guild Sci. and Techn.*, 1912, 144.

[2] *Chemist and Druggist*, September 21, 1901.

[3] *J. Soc. Chem. Ind.*, 1901, xx., 1083.

[4] *Pharm. J.*, 1920, civ., 139.

[5] Schädler, *Technologie der Fette*, 562.

has a bland taste, recalling that of almond oil, and forms a good salad oil.

It resembles ben oil in not becoming rancid for a long time after exposure to the air.

It contains no free fatty acids.

CLASS II.—RAPE (COLZA) CLASS.

BLACK MUSTARD-SEED OIL.

Recorded Values.

Black Mustard-Seed Oil.

Specific Gravity.	Acid Value.	Saponification Value.	Hehner Value.	Iodine Value.	Maumené Test.	Refractive Index.	Authority.
					°C.		
...	...	...	...	103·07	58·5	...	Lengfeld and Paparelli.
0·9161	...	174·68	...	103·57	...	1·4760	Blasdale.
0·9155 to 0·9185 at 15·5° C.	5·72 to 7·35	173·0 to 173·3	96·05	98·8 to 110·5	...	1·4655 [59·5°]	Crossley and Le Sueur.
0·9 70 to 0·9175	...	174·0 to 174·6	...	106·3 to 106·6	42 to 43	...	De Negri & Fabris.
0·920	...	181 to 181·9	...	114·9 to 120	...	...	Shukoff (*a*).

(*a*) Russian oil.

Fatty Acids.

Solidification Point.	Melting Point.	Iodine Value.	Authority.
°C. Dalican's Test.	°C.		
..	16 to 17	109·6	De Negri and Fabris.
13·4 to 13·7	..	..	Shukoff (*a*).

(*a*) Russian oil.

This oil is obtained from the seeds of the mustard plant, *Sinapis nigra*, which contain about 30 per cent.

It is light brown in colour, and has a sharp acrid smell due to the essential oil of mustard.

It is obtained as a by-product in the manufacture of mustard, and is chiefly used as a lamp oil.

The variety of mustard plant from which the oil examined by *Shukoff* was obtained is not mentioned in the original publication.[1]

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[1] *Chem. Rev. Fett Ind.*, 1901, viii., 250.

OIL OF ERUCA SATIVA.[1]

Recorded Values.

Eruca Sativa Oil.

Specific Gravity at 15·5° C.	Acid Value.	Saponification Value.	Iodine Value.	Reichert Value.	Hehner Value.	Viscosity compared with Water at 70° F.	Refraction at 40° C.		Authority.
							Scale Divisions.	Refractive Index.	
0·9177	2·10	170·4	99·72	0·66	95·49	14·61	..	..	Crossley and Le Sueur.
0·9152	3·70	169·0	97·41	0·11	..	15·93	59·2	1·4653	,,
0·9165	2·51	174·1	99·1	0·77	..	14·54	..	..	,,
0·9198	..	174·4	101·8	..	95·31	..	..	1·4723 at 20° C.	Grimme.

The plant, *Eruca sativa*, from which this oil is obtained, is allied to the mustard plants.

It is extensively cultivated in different parts of India, where the oil is used for burning, etc.; to a less extent as a food.

The three samples examined by *Crossley* and *Le Sueur* varied in colour from pale yellow to brown.

In its general characteristics the oil resembles the oils obtained from the seeds of the different mustard plants, but is a non-drying oil.

INDIAN MUSTARD-SEED OIL.[1]

Recorded Values.

Indian Mustard-Seed Oil.

Specific Gravity at 15·5° C.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Viscosity compared with Water at 70° F.	Refraction at 40° C.		Authority.
							Scale Divisions.	Refractive Index.	
0·9206	3·72	180·1	108·29	0·89	...	15·08	...		Crossley and Le Sueur.
0·9158	7·12	172·1	101·82	0·33	95·49	14·93	60·0	1·4659	,,

This oil is obtained from the seeds of the Indian mustard plant, *Brassica juncea*.

It is pale yellow in colour, has a slight odour and taste, and resembles the other mustard-seed oils in its chemical and physical characteristics.

According to *Le Sueur* and *Crossley*, the natives of India use it as an edible and medicinal oil.

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[1] Crossley and Le Sueur, *J. Soc. Chem. Ind.*, 1898, xvii., 992.

RADISH-SEED OIL.

Recorded Values.

Radish-Seed Oil.

Specific Gravity at 15° C.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Refractive Index at 40° C.	Solidification Point.	Authority.
							°C.	
0·9175	...	...	...	...	...	..	−10 to −17·5	Schädler.
0·9175	...	178·05	95·6 to 95·9	...	...	...	...	De Negri & Fabris.
0·9163 at 15·5°	14·47	173·8	92·85	0·33	95·94	1·4642 [57·5°]	...	Crossley and Le Sueur.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
°C.	°C.		
20	13 to 15	97·1	De Negri and Fabris.

This oil is obtained from the seeds of the radish, *Raphanus sativus*. It closely resembles rape-seed oil in its general characteristics, but has less drying capacity.

According to *Crossley* and *Le Sueur*,[1] it is used for food and as a lamp oil in India.

Source.—Several species of *Brassica* exist, and several varieties of the rape plant have been developed by successive cultivations; the oils from these are generally termed indiscriminately "rape" or "colza" oils in Britain. On the Continent, however, the different kinds are still frequently distinguished by separate names. Thus *Schädler* divides these oils into three classes, viz.:—

Colza oil (Colzaoel or Kohlsaatoel) from the original plant, "Kohlsaat" (*Brassica campestris*).

Rape-seed oil (Rapsoel or Rapsamenoel) from a developed variety, "Raps" (*Brassica campestris* var. *napus*, *Brassica napus oleifera*).

Rübsen oil (Rüboel or Rübsenoel) from a different variety, "Rübsen" (*Brassica campestris* var. *rapa*, or *Brassica rapa oleifera*).

Each class is further subdivided according as the plant is an annual or a biennial, the former yielding "summer oils," and the latter "winter oils." Thus—

Winter rape-seed oil from winter raps	(*Brassica napus oleifera biennis*).
Summer ,, ,, summer raps	(,, ,, *annua*).
Winter rübsen oil from winter rübsen	(*B. rapa oleifera biennis*).
Summer ,, ,, summer rübsen	(,, ,, *annua*).

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[1] *J. Soc. Chem. Ind.*, 1898, xvii., 992.

RAPE OIL, OR COLZA OIL.

Recorded Values.

Rape Oil.

Origin.	Specific Gravity at 15° C.	Hehner Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Viscosity.	Oleorefractometer at 22° C.	Refractive Index.	Authority
Commercial (52 samples),	0·9132-0·9159	...	170 -176·4	100·8-102·4	...	...	...	...	Archbutt.
,,	0·915 -0·917	...	175 -177	97·6-102·1	...	...	...	...	De Negri and Fabris.
,,	0·9133-0·9168 (at 15·5 C.)	...	170·6-175·3	99·1-105·6	...	...	...	...	Thomson and Ballantyne.
Russian,	0·916 -0·919	...	175·5-181	94·3-110·4	...	...	...	...	Shukoff.[1]
...	0·914 -0·917	...	175 -179	...	...	...	...	...	Allen.
Indian (*a*) (6 samples),	0·9141-0·9171	94·5-96·3	169·4-173·4	94·1-104·8	0·0-0·79	No. of Seconds' Flow, 50 c.c. 371·8-464·6	...	1·4659	Crossley and Le Sueur.[2]
,, (*b*)	0·9146	95·5	167·7	97·7	0·0	398	...	1·4650	,,
Commercial,	0·9140	95·6	177·8	99·1	...	100	...	...	Gripper.[3]
Commercial (8¾ years old),	0·9536	89·1	197·2	63·9	20·2	1163¼	...	...	,,
Commercial (blown),	0·9674	88·4	207·5	65·3	8·8	1886	...	...	,,
...	...	...	...	...	...	...	...	1·4667 at 60° C.	Thoerner.
Commercial (8 samples),	...	...	...	...	...	...	+16·0-20	...	Pearmain.

(*a*) *Brassica campestris.* (*b*) *Brassica napus.*

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[1] *Chem. Rev. Fett Ind.*, 1901, viii., 229.

[2] *J. Soc. Chem. Ind.*, 1898, xvii., 992.

[3] *Ibid.*, 1899, xvii., 342.

Fatty Acids.

Origin.	Specific Gravity.	Melting Point.	Solidification Point.	Iodine Value.	Mean Molecular Equiv.	Acetyl Value.	Iodine Value of Liq. Acids.	Authority.
		°C.	°C.					
...	0·8758 at 100° C. (Water 100 = 1)	18·5 to 21	...	...	...	...	...	Archbutt.
...		16 to 19	...	96·3 to 99	...	...	...	De Negri & Fabris.
Russian,	...	...	13·5 to 16·5	99·8 to 103·1	...	...	...	Shukoff.
...	0·8438 at 99° C. (Water 15·5° = 1)	18·3 to 19·5	18·5	...	321·2	...	...	Allen.
Commercial,	...	20	....	..	...	23·1	...	Gripper.
Commercial (8¾ years old),	..	21·4	...	72·1	...	41·7	...	,,
Commercial (blown),	..	...	...	...	..	42·9	...	,,
...	...	...	Dalican's Test. 11·7 to 13·6	...	...	17·2	...	Lewkowitsch.
...	...	..	...	...	...	...	120·7	Wallenstein and Fink.

Brassica nigra and *Brassica alba* are now more usually designated *Sinapis nigra* and *Sinapis alba* respectively (black and white mustard), being plants different in many respects from the cole or kohl, the seeds of which (Kohlsaat) furnish the term "colza" by corruption. Similarly, the allied *Brassica juncea* is now generally known as *Sinapis juncea*, and *Brassica chinensis* (Chinese cabbage) as *Sinapis chinensis*. Rape and colza oils are largely used in the manufacture of soft soap, leather, etc., and also for burning and as lubricants.

Expression.—Cole or rape-seed is largely cultivated in various parts of Europe, especially France, Belgium, Germany, and Hungary; also in Roumania, Russia, India, and China. Much is shipped from the Black Sea and Baltic ports, the expression being usually carried out in large mills after the fashion described in Chap. IX., the seeds being crushed between rollers, steamed to coagulate mucilage and render the oil more fluid, and subjected to hydraulic pressure before cooling.

The yield is usually from 30 to 45 per cent. according to the variety employed. *Schädler* gives the following averages:—

Summer rübsen and summer raps, ...	30 to 35 per cent.
Winter ,, winter ,, ...	35 to 40 ,,
Winter colza, ...	35 to 45 ,,

Much mucilage accompanies the crude oil; this is generally eliminated by the sulphuric acid refining process (p. 345), in some cases supplemented by an alkaline treatment to get rid of free acid, which would be injurious for lubrication purposes.

Composition.—*Reimer* and *Will*[1] came to the conclusion that the principal liquid fatty acid of rape oil was rapic acid ($C_{18}H_{34}O_3$). It was subsequently found by *Zellner*[2] that this rapic acid was really isomeric with oleic acid, and possessed the formula $C_{18}H_{34}O_2$.

According to *Ponzio*[3] rape oil contains erucic and rapic acids in approximately equal amounts. He also identified arachidic acid in the proportion of about 0·4 per cent.

Archbutt[4] has confirmed the occurrence of arachidic acid in rape oil, and has shown that the mixture of arachidic and lignoceric acid obtained in Renard's test may amount to as much as 1·43 per cent.

The mixed fatty acids on treatment with bromine resemble the acids of linseed and fish oils in giving a deposit insoluble in ether. Thus, *Hehner* and *Mitchell*[5] obtained 3·6 per cent. of an insoluble bromo-acid containing 58·6 per cent. of bromine, and having a melting point of 179° C. Rape oil, therefore, contains a highly unsaturated fatty acid, which is apparently neither linolenic nor linolic acid.

Farnsteiner[6] also separated an insoluble bromide, which, from its melting point (178° C.), he regarded as linolenic hexabromide. Obviously this was the same compound isolated by *Hehner* and *Mitchell*, in which the percentage of bromine was too small to agree with the requirements of linolenic hexabromide (63·31 per cent. of bromine, m.p. 181° C.).

Rape oil itself yields a fine granular insoluble precipitate on treatment with bromine, analogous to that obtained with linseed oil. The yield is about 1 per cent. (*Hehner* and *Mitchell*, *loc. cit.*).

On standing for a long period a solid deposit separates from rape oil. According to *Halenke* and *Möslinger* a specimen of this deposit had characteristics corresponding to nearly pure trierucin, whereas *Reimer* and *Will* came to the conclusion that the deposit from old oils consisted of dierucin.

Unsaponifiable Matter.—Rape oil contains less than 1 per cent. of unsaponifiable matter (phytosterol, etc.). A determination of this constituent will afford information as to the presence of mineral oils. In one specimen of oil *Fahrion* found 1·48 per cent. unsaponifiable matter.

Free Fatty Acids.—*Thomson* and *Ballantyne* found from 2·4 to 6·2 per cent. of free acids (as oleic) in various commercial samples of rape oil. The Indian rape oils examined by *Crossley* and *Le Sueur* contained 0·36 to 1 per cent., whilst in Russian oils *Shukoff* found from 0·95 to 9·5 per cent.

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[1] *Ber. d. d. chem. Ges.*, 1887, xx., 2388.

[2] *J. Soc. Chem. Ind.*, 1896, xv., 661.

[3] *Ibid.*, 1894, xiii., 257.

[4] *Ibid.*, 1898, xvii., 1009.

[5] *Analyst*, 1898, xxiii., 317.

[6] *Zeit. Untersuch. Nahr. Genussm.*, 1899, ii., 1.

Sulphur in Rape Oil.—The presence of a considerable proportion of sulphur was at one time regarded as a characteristic of rape-seed and other oils from the *Cruciferæ*. *De Negri* and *Fabris*, however, have found that sulphur is not an invariable constituent of rape oil, and also that all oils extracted with carbon bisulphide contain sulphur, so that no reliance can be placed upon the test.

Change in Composition on Keeping.—*Gripper* (*loc. cit.*) has examined a number of samples of rape oil that had been kept for some years, and shows that the changes in composition are similar to those brought about by "blowing" rape oil. The comparative results obtained with one sample of old oil and of ordinary and blown oils are shown in the table of recorded values (*supra*).

From these results it appears that on spontaneous or artificial oxidation of rape oil there is an increase in the specific gravity and viscosity, and a decrease in the iodine value. There is also an increase in the proportion of soluble fatty acids, and, eventually, in the acetyl value of the insoluble fatty acids. The main difference between the spontaneously oxidised and the blown oils is that the former contain a larger proportion of volatile fatty acids.

Properties.—Rape oil varies in colour from very pale yellow or dark yellow, and has a characteristic smell and taste.

It is not possible to distinguish between the different kinds of rape oil obtained from the varieties of *Brassica campestris* mentioned above, the physical and chemical characteristics being very similar.

Solidification Point.—*Holde* and *Ruhemann*[1] found that nearly all the different rape oils solidified after standing for about eight hours at 0° C. They attributed the lower figures recorded (*e.g.*, − 4, *Hübl*; − 1 to − 10, *Schädler*; − 2 to − 10, *Benedikt*) to the oil not being shaken during the cooling process.

Saponification Value.—The presence of a considerable proportion of erucin causes rape oil to have a remarkably low saponification value. This property is a valuable criterion of purity, since the usual adulterants of rape oil have much higher saponification values. Oils of similar character to rape oil, such as mustard-seed oil and radish oil, have equally low saponification values, but are unlikely to be used for purposes of adulteration.

Drying Properties.—Rape oil dries very slowly, becoming more viscous, but not yielding a solid film. In Bishop's test it absorbed about 5·8 per cent. of oxygen, or slightly more than olive oil. Tested by Livache's method rape oil gained 2·9 per cent. in weight after seven days' exposure, whilst the fatty acids gained 0·9 per cent. in eight days (see Chap. VII.).

Iodine and Bromine Values.—In addition to the values given in the table of recorded values, mention may be made of the results

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[1] *J. Soc. Chem. Ind.*, 1896, xv., 122.

obtained by *Wijs*[1]—viz., 102·96 by Hübl's method (four hours), and 103·3 by Wijs' method (seven minutes).

There appears to be more substitution with iodine than with bromine, since the following results were obtained by *Vulté* and *Logan*[2]:—

Iodine Value *(Hübl)*.	Iodine Value calculated from Bromine Value.
103·4 to 103·7	98·6 to 99

The addition of linseed or other highly unsaturated oils to rape oil will be shown by an increase in the iodine value.

Maumené Test.—The following results have been recorded:—57° to 58° C. (*Maumené*), 55° to 64° (*Archbutt*), 51° to 60° (*Allen*), 49° to 51° (*De Negri* and *Fabris*). Specific temperature reaction, 125° to 144° (*Thomson* and *Ballantyne*).

In Mitchell's method of applying the test there is an approximate correspondence between the halogen standard figures and bromine thermal values both in the case of rape oil and of its free fatty acids (see *Maumené Test*, Chap. VII.).

Solubility in Different Solvents.—Refined rape oil is slightly soluble in alcohol (about 0·5 part in 100 parts).

Crismer and *Motteu*[3] found the *critical temperature of solution* in alcohol of specific gravity 0·8195 to range from 132° to 135° C.

The solubility in acetic acid varies considerably according to the proportion of free fatty acids. Thus, *Chattaway*, *Pearmain*, and *Moor*[4] obtained results in the Valenta test of 63·0° to 78° C. with four specimens of rape oil, and of 83° C. with a sample of German colza oil.

Viscosity.—Rape oil is distinguished by its very high viscosity, and this property is a valuable test of its purity. For values in addition to those given in the Table of Values, see Chap. V.

Detection of Adulteration.—Among the oils used for adulterating rape oil are linseed, cotton-seed, hemp-seed, poppy, fish, mineral, and resin oils.

Linseed Oil will be indicated by a higher iodine value, and by yielding a larger proportion of insoluble bromine compounds.

Cotton-seed Oil causes the fatty acids to melt at a higher temperature, and raises the iodine value. Becchi's and Halphen's reactions will also be valuable.

Fish Oils raise the iodine value and yield insoluble bromides. Their fatty acids have also a characteristic smell, which is more perceptible on heating. The detection of cholesterol in the unsaponifiable matter will also point to the presence of an oil of animal origin.

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[1] *Ber. d. d. chem. Ges.*, 1898, xxxi., 750.

[2] *J. Amer. Chem. Soc.*, 1901, xxiii., 158.

[3] *Bull. de l'Ass. belge Chim.*, 1896, ix., 359.

[4] *Analyst*, 1894, xix., 150.

WHITE MUSTARD-SEED OIL.

Recorded Values.

White Mustard-Seed Oil.

Specific Gravity.	Acid Value.	Saponification Value.	Hehner Value.	Iodine Value.	Maumené Test.	Refractive Index.	Solidification Point.	Authority.
					° C.		° C.	
...	...	...	96·70	97·68	49·5	...	...	Lengfeld and Paparelli.
0·9151	...	173·94	...	98·41	...	1·4751	...	Blasdale.
0·9142 at 15·5° C.	5·4	171·20	95·86	96·75	...	1·4649 [58·5°]	...	Crossley and Le Sueur.
...	...	...	...	92·1 to 93·8	44 to 45	...	...	De Negri & Fabris.
0·9125 to 0·9160	...	170·3 to 171·4	...	...	...	...	...	——
0·9145	...	...	...	...	...	...	− 8 to − 16	Schädler.

Fatty Acids.

Melting Point.	Iodine Value.	Authority.
° C.		
16	...	Blasdale.
15 to 16	94·7 to 95·8	De Negri and Fabris.

This oil, obtained from the seeds of *Sinapis alba*, is used for lubricating and illuminating purposes.

It contains arachidic acid in small quantity. *Archbutt*[1] separated 1·18 per cent. of the mixed arachidic and lignoceric acids (m.p. 69° C.) from a specimen of the oil.

Mustard-seed oil resembles linseed oil in yielding an insoluble derivative on treatment with bromine, possibly the bromide of a mixed glyceride containing linolenic acid. The amount of fine granular precipitate thus obtained by *Hehner* and *Mitchell*[2] from a sample of the oil was 1·5 per cent.

White mustard-seed oil is very similar to the black mustard oil in its chemical and physical properties, excepting that, as a rule, its iodine value is considerably lower.

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[1] *J. Soc. Chem. Ind.*, 1898, xvii., 1009.

[2] *Analyst*, 1898, xxiii., 317.

CLASS III.—CASTOR OIL CLASS

CASTOR OIL.

Recorded Values.

Castor Oil.

Origin.	Specific Gravity.	Reichert Value	Saponification Value.	Iodine Value.	Acetyl Value.	Refractive Index.	Authority.
...	0·960 to 0·966 at 15·5° C.	1·4	176 to 178	...	...	...	Allen.
Indian (23)	0·9637 to 0·9642	...	176·7 to 179·1	[52·9 to 53·7] (Bromine value.)	...	Oleorefractometer. +41·0 to 42·5	Deering and Redwood.[1]
...	...	...	183·3	...	149·9 150·5	...	Lewkowitsch.
...	...	...	...	...	...	1·4636 at 60° C.	Thoerner.
...	0·960 to 0·967	...	175 to 182	...	about 150	Refractometer. +39 to 42 at 22° C.	Dowzard.
Russian, medicinal.	0·9655	...	178	84	...	...	Shukoff.[2]
American	0·967	...	...	84·1	...	...	Sherman and Snell.[3]

Fatty Acids.

Specific Gravity.	Melting Point.	Solidification Point.	Iodine Value.	Refractive Index.	Authority.
0·9509 at 15° C. 0·8960 at 98° to 99° C.	...	...	...	...	Allen.
...	...	...	87 to 88	1·4546 at 60° C.	Thoerner.
...	13° C.	3° C.	...	...	Hübl.
...	...	Turbid, but not solid, at −15° C.	...	...	Mitchell.
...	...	. .	Liquid Fatty Acids. 96·27	...	Lane.

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[1] *J. Soc. Chem. Ind.*, 1894, xiii., 959.

[2] *Chem. Rev. Fett Ind.*, 1901, viii., 250.

[3] *J. Amer. Chem. Soc.*, 1901, xxiii., 164.

Source.—Castor oil is obtained from the seeds of *Ricinus communis*, which is cultivated in India, Java, the countries surrounding the Mediterranean, the Azores, and elsewhere.

A large proportion of the castor oil of commerce is prepared at Marseilles, though of late years Marseilles has had to meet competition from mills in Lancashire and in the North of Europe. According to a *Board of Trade Report* (Commercial Department, August 10, 1901), the superior quality of Marseilles medicinal oil is to be attributed to the climate and the sunshine which accelerates the bleaching of the oil.

Pharmaceutical oil is also manufactured in India, in Germany (Mannheim), and in the United States.

As prepared in Marseilles, the seed is shelled, crushed in hydraulic presses, and clarified by filtration, this oil being suitable for technical purposes. In the second pressing a certain proportion of water is added.

The residual oil-cake (about 60 per cent. of the seed) is in great demand for manure in the neighbourhood of Marseilles, and cake of British manufacture has even been offered for sale there, there being no demand for it in this country.

There is now an enormous demand for castor oil for the engines of aircraft, and this has resulted in the development of the industry, especially in the United States.[1]

The U.S.A. War Dept. specifies that castor oil for lubricating engines must be colourless; sp. gr., 0·959 to 0·968 at 60° F.; completely soluble in 4 volumes of 90 per cent. alcohol (sp. gr. 0·834) at 60° F.; maximum acidity = 1·5 per cent. oleic acid; iodine value, 80 to 90; saponification value, 176-187; unsaponifiable matter, below 1 per cent. It must be free from rosin, rosin oil, or cotton-seed oil. Viscosity (Saybolt), 450 secs. at 130° F., or 95 secs. at 212° F.; flash-point, 459° in a Cleveland open cup; freezing-point, below zero F.

Composition.—According to *Ure* castor oil has the following elementary composition:—Carbon, 74·00; hydrogen, 10·26; oxygen, 15·71.

It consists mainly of triricinolein, with a small proportion of glycerides of solid fatty acids. According to *Krafft* castor oil, when exposed for a long time to a low temperature, yields 3 to 4 per cent. of a solid deposit consisting of stearin and triricinolein, the fluid ricinolein in the oil being, in his opinion, in a state of superfusion.

When the fatty acids of castor oil are kept for a long time at 12° C. a crystalline deposit is obtained, which, when crystallised from alcohol, yields a mixture of stearic acid and dihydroxystearic acid. The stearic acid can be removed by means of hot benzene, and the residual dihydroxystearic acid recrystallised from alcohol. It melts at 141° to 143° C., and forms about 1 per cent. of the castor oil (*Juillard*).[2]

Hazura and *Grüssner*[3] found crude ricinoleic acid to consist of

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[1] See *J. Soc. Chem. Ind.*, 1919, xxxviii., 20 R.

[2] *Bull. Soc. Chim.*, 1895, xiii., 238.

[3] *Monatsh. f. Chem.*, ix., 475

two isomeric acids, ricinoleic and isoricinoleic acid, the former yielding trihydroxystearic acid (m.p. 140° to 142° C.), and the latter isotrihydroxystearic acid (m.p. 110° to 111° C.) on oxidation with alkaline permanganate.

Fahrion isolated 0·59 per cent. of unsaponifiable matter from a sample of castor oil.

Distillation Products of Castor Oil.—Towards the end of the distillation the contents of the retort are suddenly converted into a viscous rubber-like mass, whilst considerable gas is evolved. *Thomas* and *Fendler*[1] find the residue to consist to a large extent of the glyceride of a dibasic fatty acid, triundecylenic acid, $(C_{11}H_{20}O_2)_3$. When heated with potassium hydroxide the residue yields a new fatty acid of the oleic series, melting at 36° C., and having the composition $C_{16}H_{30}O_2$.

Artificial Castor Oil.—*Juillard*[2] prepared an "artificial castor oil" by heating ricinoleic acid with glycerol for six hours in an oil-bath at 230° C. He found the mixture thus obtained to consist mainly of triricinolein (2 molecules) and diricinolein (1 molecule). Its molecular weight was found by Raoult's method to be 836, the calculated figure being 838.

Meyer[3] considers that Juillard's artificial glyceride must have been nearly pure diricinolein. Unlike the natural glyceride it does not form solid ricinelaidin. After about a year the molecule appears to be doubled or tripled, the specific gravity being increased from 0·988 to 1·009, and the iodine value reduced from 71·84 to 44·57. Its optical rotation is $(\alpha)_D = +5° 16'$. It is soluble in an equal volume of alcohol, and has the aperient properties of castor oil.

Ethyl Esters of Castor Oil.—*Henriques*[4] readily obtained these by saponifying castor oil with 15 per cent. of the theoretical amount of alcoholic potassium hydroxide. When separated by distillation and dried in a current of carbon dioxide these esters had the following characteristics:—Saponification value, 174·9; iodine value, 84·1. They were less viscous than the original oil, and dissolved completely, though not readily, in petroleum spirit. They had the same taste and physiological properties as castor oil.

Active Physiological Constituent.—*Meyer*[5] states that the purgative action of castor oil is not weakened by treating the oil with hydrochloric acid gas, or by exposure to a temperature of 300° C. On the other hand, ricinoleic acid loses its purgative property when treated with mineral acids, being converted into ψ-ricinoleic acid, which is physiologically inactive. In Meyer's opinion the action of castor oil is due to the ricinoleic acid.

Ricinelaidic acid and ricinelaidin are in themselves inactive, but in the form of a solution or emulsion have marked aperient properties (*Meyer*).[6]

Solidification Point.—Castor oil becomes turbid at − 12° C., and solidifies at − 17° to − 18° C. According to *Schädler*[7] the American oil, which contains more "stearine," solidifies at − 10° to − 12° C. A specimen of castor oil examined by the present writer (*M.*) remained perfectly clear at − 15° C.

Solubility in other Liquids—*Alcohol.*—A characteristic property of castor oil is its great solubility in absolute alcohol. At 15° C. 1 part of the oil is soluble in 2 parts of 90 per cent. alcohol (sp. gr. 0·9228), and in 4 parts of 84 per cent. alcohol (sp. gr. 0·9338).[8]

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[1] *Arch. Pharm.*, 1901, 1.

[2] *Bull. Soc. Chim.*, 1895, xiii., 240.

[3] *Zeit. angew. Chem.*, 1897, 297.

[4] *Zeit. angew. Chem.*, 1898, 338.

[5] *Chem. Centralbl.*, 1897, i., 591.

[6] *Pharm. Zeit.*, 1897, xlii., 326.

[7] *Technologie der Fette*, 554.

[8] Schädler, *loc. cit.*

Finkener[1] recommends the following test:—10 c.c. of the oil are shaken with 50 c.c. of alcohol (sp. gr. 0·829) in a stoppered cylinder, which is left for two to three minutes. A strong turbidity, which does not disappear at 20° C., points to the presence of at least 10 per cent. of other oils.

Chercheffsky[2] determines the turbidity temperature of 8 drops of oil in 40 drops of alcohol (sp. gr. 0·8481 at 15°/15° C.) in a sealed tube (see *Critical Temperature of Solution*, p. 72). Pure castor oil gives a turbidity temperature of 66° to 67°, whilst the addition of 2 per cent. of arachis, linseed, fish, or rape oil raises the value to 69°-71° C. If necessary free fatty acids must first be removed by washing the oil with dilute alkali solution.

For the detection of foreign oils in castor oil, which is now extensively used for lubricating aeroplane engines, *Frabot*[3] determines the turbidity temperature of 1 volume in 5 volumes of 95 per cent. alcohol. In the case of pure castor oil the solution can be cooled below − 20° C. without solidifying, whereas in the presence of arachis oil the liquid becomes turbid at temperatures varying with the proportion of foreign oil.

Petroleum Spirit.—Castor oil is insoluble in petroleum spirit and other mineral oil. In Hager's opinion an oil that gives a turbidity with petroleum spirit whilst dissolving to a clear solution in 5 parts of 90 per cent. alcohol may be regarded as pure.

Acetic Acid.—Castor oil is readily soluble in glacial acetic acid (*cf. Valenta's Test*).

Acidity.—Freshly-expressed castor oil contains but little free acid. *Sherman* and *Snell* found a sample to contain 0·82 per cent. (as oleic acid), whilst *Shukoff* found 0·41 per cent. in Russian oil. The acid value of the twenty-three Indian oils examined by *Deering* and *Redwood* varied from 0·12 to 1·23 per cent.

Bromine and Iodine Values.—Castor oil has a considerable bromine substitution figure, as is shown by the following results obtained by *Vulté* and *Logan*:—[4]

Iodine Value (*Hübl*).	Total Bromine Absorption.	Addition Figure.	Substitution Figure.	Iodine Value Calculated from Bromine.
86·32 to 87·15	52·62 to 52·80	50·09 to 50·07	2·53 to 2·73	78·74 to 78·71

Jenkins[5] gives the following comparative figures, in which the

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[1] *J. Soc. Chem. Ind.*, 1887, vi., 148.

[2] *Ann. Chim. Anal.*, 1918, xxiii., 75.

[3] *Ibid.*, 1917, xxii., 217.

[4] *J. Amer. Chem. Soc.*, 1901, xxiii., 156.

[5] *J. Soc. Chem. Ind.*, 1897, xvi., 193.

bromine values are calculated into the corresponding iodine values :—

Iodine Value (*Hübl*).	Iodine Value Calculated from Bromine Thermal Value.	Iodine Value Calculated from Bromine Gravimetric.			
		Dried at 97° C.		Dried at 125° C.	
		3 Hours.	5 Hours.	5 Hours.	10 Hours.
84·1	83·8	88·8	86·9	80·0	77·2

Maumené Test.—The following figures, obtained by the older method, have been recorded :—47 (*Maumené*), 46 (*Archbutt*).

Specific temperature reaction, 105 (*Jenkins*).

Castor oil resembles boiled and oxidised oils in giving Maumené figures by Mitchell's method[1] considerably higher than the values calculated from the bromine thermal value.

Viscosity.—Castor oil is distinguished from other fresh oils by its great viscosity, in which it is only approached by oxidised oils, and from these it differs in its high acetyl value.

Deering and *Redwood* (*loc. cit.*) obtained readings varying from 1,160 to 1,190 seconds for 50 c.c. in a Redwood's viscosimeter at 100° F., and similar readings were obtained by *Dowzard*.[2]

The "mobility" of castor oil, examined by Weiss's mobility test (*q.v.*), increases with the rise in temperature, in which respect it differs from other oils.

Heat of Combustion.—Castor oil gives a low heat of combustion as compared with other oils, the results being similar to those given by boiled linseed oil and oils that have undergone spontaneous oxidation on keeping. Thus *Sherman* and *Snell* (*loc. cit.*) obtained the following results :—Castor oil, 8,863 ; linseed oil, 9,364 ; boiled linseed oil, 8,810 ; cotton-seed oil, 9,396 ; and old cotton-seed oil, 9,168 calories per gramme.

Acetyl Value.—In addition to the values in the table of constants, *Lewkowitsch*[3] obtained a value of 146·9 for fresh castor oil, and of 144·8 for oil that had been exposed to the atmosphere.

This high acetyl value distinguishes castor oil from all commonly occurring oils, with the exception of grape-seed oil, which also has a very high value.

Elaidin Reaction.—Castor oil yields a white solid mass after six to eight hours, owing to the formation of ricinelaidin.

Detection of Adulteration.—The most reliable tests of the purity of castor oil are the determination of the acetyl value and its behaviour with alcohol and petroleum spirit. Useful information will also be

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[1] *Analyst*, 1901, xxvi., 171.

[2] *Chemist and Druggist*, 1901, lviii., 325.

[3] *Analyst*, 1899, xxiv., 327.

afforded by the low saponification value, iodine value, the extremely low melting point of the mixed fatty acids, the high specific gravity, viscosity, and optical rotation.

CURCAS OIL.

Recorded Values.

Curcas Oil.

Specific Gravity.	Hehner Value.	Saponification Value.	Reichert Value.	Iodine Value.	Acetyl Value.	Refractive Index at 25° C.	Authority.
0·9192	...	230·5	0·65	127·0	...	...	Horn.[1]
0·920	...	210·2	...	100·9	...	...	De Negri & Fabris.[2]
0·925 (*a*)	...	192·8	...	98·0	14·03	...	Archbutt.[3]
			Reichert-Meissl.				
0·9205 (*b*)	95·2	192·5	0·28	99·5	9·82	...	,,
0·9205 (*b*)	...	192·6	0·48	98·8	8·36	...	,,
0·9210 (*c*)	...	203·5	...	109·8	...	1·4686	Klein.[4]
0·9240 (*d*)	...	203·6	...	109·1	17·6 & 25·3	1·4689	,,
0·9199 (*e*)	...	197·5	...	110·4		1·4687	,,
0·9207 (*e*)	...	197·0	...	109·1	...	1·4687	,,
0·9208 (*f*)	...	198·1	...	107·9	...	1·4680	,,

(*a*) Crude, (*b*) refined, (*c*) cold-pressed oil, (*d*) hot-pressed, (*e*) cold-pressed, (*f*) commercial, hot-pressed.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
° C.	° C.		
24 to 26	...	105·05	De Negri and Fabris.
27·5	...	...	Archbutt.
29·5	25·75	...	Klein.
30·5	26·5	...	,,

Source.—Curcas oil is obtained from the seeds of the "physic-nut" tree, *Jatropha curcas*, whch resembles the castor oil plant in appearance. It is specially cultivated in the Portuguese Colonies, whence the bulk of the seed is exported to Lisbon and expressed.

It is chiefly used for lubricating and illuminating purposes and in the manufacture of soap and candles. It has marked purgative properties, and in India is used medicinally. According to *Klein* 10

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[1] *J. Soc. Chem. Ind.*, 1888, vii., 442.

[2] *Ibid.*, 1893, xii., 453.

[3] *Ibid.*, 1898, xvii., 1010.

[4] *Zeit. angew. Chem.*, 1898, 1012.

drops of curcas oil have as strong a purgative effect as a tablespoonful of castor oil.

Composition.—*Klein* (*loc. cit.*) found a specimen to contain 9 to 10 per cent. of solid fatty acids consisting of 80 per cent. of palmitic acid and 20 per cent. of stearic acid, no myristic acid being present. The liquid acids consisted of equal parts of oleic and linolic acids, no linolenic or ricinoleic acid being present. The amount of phytosterol was 0·58 per cent.

Properties.—Curcas oil has a characteristic odour, and varies in colour from yellowish-red to red according to the degree of heat and pressure used for its extraction.

Solubility.—It is much less soluble than castor oil in cold alcohol (1 : 100 of 96 per cent. strength, *De Negri* and *Fabris*), but readily dissolves in petroleum spirit.

Arnaudon and *Ubaldini*[1] found that on treating curcas oil with successive small portions of cold alcohol a small quantity of insoluble residue remained.

Solidification Point.—A specimen of refined oil examined by *Archbutt* became turbid at 4·4° C., and solidified at 2·8° to 2·9° C.

Free Fatty Acids.—*Klein* found the amount of free fatty acids to vary from 0·57 to 4·96 per cent. in five specimens of oil obtained by different methods, whilst *Archbutt* obtained results ranging from 0·36 to 11·8 per cent. (as oleic acid) in the case of the three oils examined by him.

Viscosity.—This lies between that of rape and of cotton-seed and olive oils. In Engler's viscosimeter *Klein* obtained the following results at 20° C.:—Curcas oil, 9·45; rape oil, 9·03; and olive oil, 10·3.

The absolute viscosity at 15·5° C. was found by *Archbutt* to vary from 0·858 to 0·878, whilst refined cotton-seed oil gave values ranging from 0·82 to 0·91, and refined rape from 1·09 to 1·16.

Drying Properties.—Curcas oil has considerable drying properties, though not so good as those of cotton-seed oil. According to *Schädler* it forms a varnish when boiled with metallic oxides.

Maumené Test.—In the Maumené test by the original method *Archbutt* obtained results varying from 65·0 to 67·5 with three specimens of the oil.

Colour Reactions.—With nitric acid it gives a pale brown colour, changing to orange, but gives no reaction with Milliau's silver nitrate test, or Halphen's or the Baudouin test.

Detection of Adulteration.—It has been asserted that curcas oil is sometimes used to adulterate olive oil, but taking into consideration its purgative properties such an addition is *a priori* unlikely. *Klein*, too, states that he has never met with such adulteration. If the oil were so used the odour, specific gravity, refractive index, and iodine value would afford indications of its presence.

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[1] *J. Soc. Chem. Ind.*, 1893, xii., 934.

The best tests for curcas oil in castor oil are the viscosity, specific gravity, iodine value, and difference in solubility.

GRAPE-SEED OIL.

Recorded Values.

Grape-Seed Oil.

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Acetyl Value.	Maumené Test.	Reichert-Meissl Value.	Hehner Value.	Solidification Point.	Authority.
				°C.			°C.	
0·9350	178-179	94·96	...	94·96	...	...	−10 to −13	De Negri & Fabris.[1]
0·9561	178·4	94	144·5 (*a*)	...	0·46	92·13	...	Horn.[2]
0·9202	...	...	...	...	...	...	−15 to −17	Schädler.

(*a*) Determined by Benedikt's original method.

Fatty Acids.

Melting Point.	Solidification Point.	Saponification Value.	Iodine Value.	Authority.
°C.	°C.			
23-25	18-20	187	98·9-99	De Negri and Fabris.
...	...	187·4	98·65	Horn.

This oil, obtained from the seeds of the grape, consists, according to *De Negri* and *Fabris*, of the glyceride of erucic acid with a little palmitin and stearin. *Lewkowitsch* considers that, inasmuch as it contains a large proportion of hydroxy fatty acids, it is very doubtful whether erucic acid is present.

The cold-drawn oil is used for food and as a lamp oil. In Horn's opinion it is preferable to castor oil for the manufacture of Turkey-red oil.

It is distinguished by having a high acetyl value, in which respect it resembles castor oil.

It is soluble in glacial acetic acid at 70° C., but the solution becomes turbid at 66·5° C.

[1] *Zeit. anal. Chem.*, 1894, xxxiii., 566.

[2] Benedikt, *Analyse der Fette.*, 2nd Ed., 362 (Extracted oil).

In the Maumené test *De Negri* and *Fabris* observed a rise of 52° to 54° C.

CLASS IV.—ANIMAL NON-DRYING OILS.

LARD OIL.

Recorded Values.

Lard Oil.

Specific Gravity.	Saponification Value.	Iodine Value.	Hehner Value.	Refractometer (*Zeiss*).	Maumené Test.	Critical Temp. of Solution (*Crismer*).	Solidification Point.	Authority.
					° C.	° C.	° C.	
0·916 at 14° C. 0·8626 at 100° C.	193	73	97·4	52° at 40° C.	47	75 (open tube)	about 10	Duyk.[1]
...	...	...	...	Oleo-refractometer at 22° C. +0·0 to 1·0	...	...	...	Pearmain.
0·917 to 0·924 at 15·5° C.	...	69·3 to 74·3	...	...	...	...	...	Sherman[2] & Snell.
...	...	...	...	...	...	104	...	Crismer.

Fatty Acids.

Specific Gravity.	Melting Point.	Solidification Point.	Authority.
	° C.	° C.	
0·885 at 100° C.	35	31	Duyk.

Lard oil is the more fluid portion obtained on subjecting lard to cold expression, whilst the hard residue is known as lard stearine (see Chap. IX., p. 314).

It consists mainly of olein, with smaller quantity of linolin, palmitin, and stearin, and is practically free from volatile fatty acid.

The four oils examined by *Sherman* and *Snell* contained from 0·74 to 2·64 per cent. of free acid (as oleic).

Owing to the large proportion of olein that it contains, lard oil rapidly yields a solid mass in the elaidin test.

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[1] *Bull. de l'Ass. belge Chim.*, 1901, xv., 18.
[2] *J. Amer. Chem. Soc.*, 1901, xxiii., 164.

NEAT'S FOOT OIL.

Recorded Values.

Neat's Foot Oil.

Specific Gravity.	Solidification Point.	Iodine Value.	Oleo-refractometer at 22° C.	Maumené Test.	Valenta Test.	Critical Temp. of Solution.	Authority.
	°C.			°C.	°C.	°C.	
...	0 to 1·5	...	...	...	...	...	Schädler.
...	...	...	...	...	...	95	Crismer.
0·914 to 0·915 at 15° C.	...	67·1 to 72·9	...	42·2 to 49·5	51·0 to 75·5	...	Gill and Rowe. (5 samples.)
...	...	...	+1 to 3	...	...	...	Pearmain.
0·915 to 0·916	10	...	...	47 to 48·5	...	...	Jean.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
°C.	°C.		
29·8 to 30·8	...	61·9 to 63·3	Jean.
...	16 to 26·5	63·6 to 69·5	Gill and Rowe.

The oil expressed from the "feet" (hoofs and hocks) of oxen is known as "neat's foot oil." It is a pale yellow, limpid liquid, which contains but little solid glycerides and is largely used for lubricating purposes (see p. 374).

It is frequently adulterated with vegetable and mineral oils.

The oils obtained from the hoofs of horses and trotters of sheep are very similar in character to neat's foot oil.

TALLOW OIL.

Recorded Values.

Tallow Oil.

Specific Gravity.	Iodine Value.	Maumené Test.	Valenta Test.	Authority.
		°C.	°C.	
0·794 at 100° C.	55·8-56·7	35·0	71·0-75·7	Gill and Rowe (3 samples).[1]

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[1] *J. Amer. Chem. Soc.*, 1902, xxiv., 466.

Fatty Acids.

Solidification Point.	Iodine Value.	Authority.
°C Dalican's Test. 35-37·5	54·6-57	Gill and Rowe.

Tallow oil is the fluid portion which is separated on subjecting beef or mutton tallow to expression (Chap. IX.).

It resembles neat's foot oil, but contains a larger proportion of saturated glycerides, and is less valuable as a lubricant.

CLASS V.—VEGETABLE SEMI-DRYING OILS.

ACORN OIL.

The oil extracted by *Blasdale*[1] with petroleum spirit from the nuts of the oak, *Quercus agrifolia*, was of a deep brown colour. It solidified at 10° C., and, on standing, deposited a wax-like substance.

It had the following constants :—

Specific gravity at 15° C., ...	0·9162
Saponification value, ...	199·26
Iodine value, ...	100·66
Maumené figure (5 c.c. oil + 15 c.c. H_2SO_4), .	60·0
Viscosity of soap solution, ...	305
Refractive index, ...	1·4731
Melting point of fatty acids, ...	25° C.

This oil did not yield any solid product in the elaidin test. It gave slight reactions in Milliau's test.

BEECH-NUT OIL.

Recorded Values.

Oil.

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Maumené Test.	Heat of Combustion. Calories per Grm.	Refractive Index at 20° C.	Solidification Point.	Authority.
						°C.	
0·9220-0·9225	191-196	104-111	63	...	...	-17	De Negri & Fabris.[2]
0·9214 at 24° C.	...	97·31	...	9511	1·4715	...	Merrill.[3]
...	...	...	65	...	...	...	Maumené.
...	196·3	104·4	...	...	...	...	Girard.

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[1] *J. Amer. Chem. Soc.*, 1895, xvii., 935.

[2] *Zeit. anal. Chem.*, 1894, xxxiii.

[3] *Maine Agric. Exper. Stat. Bull.*, 1900, [65], 111.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
° C.	° C.		
23	...	114	De Negri and Fabris.
24	17	...	Girard.

This oil is obtained from the nuts of the beech tree (*Fagus sylvatica. F. Americana*).

According to *De Negri* and *Fabris*, it is frequently used to adulterate almond oil, since it does not readily become rancid, whilst oil of the second expression is used for burning and in the manufacture of soap.

It contains olein and linolin (probably), with a little palmitin and stearin.

On treatment with dilute nitric acid (3 : 1), it gives an orange coloration and eventually a solid elaidin.

Its presence in almond oil would be indicated by this test, and by the increase in the iodine value.

BRAZIL-NUT OIL.

Recorded Values.

Brazil-Nut Oil.

Specific Gravity at 15° C.	Acid Value as Oleic Acid.	Saponification Value.	Iodine Value.	Refractive Index at 20° C.	Solidification Point.	Heat of Combustion. Calories per Grm.	Authority.
	Per cent.				° C.		
0·9170-0·9185	..	193	95-106	...	0 to + 3	...	De Negri and Fabris.[1]
0·918	1·433	193·4	106·22	..	0	...	De Negri.[2]
0·9156 at 24° C.	...	...	90·59	1·4699	...	9426	Merrill.[3]

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
° C.	° C. Dalican's Test.		
...	...	...	De Negri and Fabris.
28-30	...	106·04	De Negri.
...	31·1-32·2	...	Lewkowitsch.

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[1] *Zeit. anal. Chem.*, 1894, xxxiii., 563.
[2] *Chem. Zeit.*, 1898, xxii., 961.
[3] *Maine Agric. Exper. Stat. Bull.*, 1900, [65], 111.

This oil is extracted from the nuts of *Bertholletia excelsa*, which grows in the South American forests.

When fresh it is nearly colourless, but on keeping becomes yellow and yields a white crystalline deposit. It readily becomes rancid.

According to *De Negri* and *Fabris*, the extracted oil has a lower iodine value (93·8 to 95·8) than the expressed oil. This statement is in agreement with the value obtained by *Merrill* with an oil extracted from the nuts with ether.

It yields no insoluble compound on treatment with bromine (*Hehner* and *Mitchell*).

CAMELINE OIL.

GERMAN SESAMÉ OIL.

Recorded Values.

Cameline Oil.

Specific Gravity.	Saponification Value.	Iodine Value.	Maumené Test.	Solidification Point.	Authority.
			°C.	°C.	
0·9260	188	135·3	117	...	De Negri and Fabris.[1]
0·9228	...	136·2	...	–18 to –19	Schädler.
...	...	132·6	...	...	Girard.
0·9270	155	152-153	...	...	Shukoff.
...	...	146	...	...	Van Ketel and Antusch.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
°C.	°C.		
18-20	13-14	136·8	De Negri and Fabris.
	Dalican's Test.		
...	17-18	...	Shukoff.

Cameline oil is obtained from the seeds of *Camelina sativa*, a plant belonging to the *Cruciferæ*. From 23 to 25 per cent. of oil is obtained by hot expression, and 28 per cent. by extraction with solvents.

It is a light yellow oil with a peculiar odour, which is also perceptible when the oil is mixed with other oils.

According to *De Negri* and *Fabris*, it contains the glycerides of oleic, linolic, and palmitic acids, with slight quantities of erucic acid.

It has weak drying properties, and occupies an intermediate position between the drying and semi-drying oils. It is used in the

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[1] *Zeit. anal. Chem.*, 1894, xxxiii., 555.

manufacture of soft soap and as an adulterant of rape oil. The oil obtained by cold expression is sometimes used for food after clarification.

Van Ketel and *Antusch*[1] show that linseed is likely to contain cameline seed, and that this accounts for the low iodine value of the oils extracted from certain linseed cakes. Thus, linseed yielding an oil with an iodine value of 187, when mixed with 20 per cent. of cameline seed yielded an oil with an iodine value of 170.

CEDAR-NUT OIL.

Recorded Values.

Cedar-Nut Oil.

Specific Gravity.	Acid Value.	Saponification Value.	Hehner Value.	Iodine Value.	Reichert-Meissl Value.	Authority.
...	1·09	191·8	93·33	149·5-150·5	2 0	Kryloff.[2]
0·930	...	191·8	91·97	159·2	...	Schmoelling.[3]
0·928	...	193·7	...	143·8	...	Shukoff.[4]

Fatty Acids.

Solidification Point.	Saponification Value.	Iodine Value.	Authority.
° C.	°C.		
11·3	193·0	161·3	Schmoelling.
Dalican's Test. 11	...	...	Shukoff.

Cedar-nut oil is obtained from the seeds of the Siberian cedar (*Pinus cembra*). It is pale yellow and of a somewhat harsh taste, though used locally as an edible oil.

A specimen examined by *Schmoelling* had the following composition :—Glycerol, 10·31 ; volatile fatty acids, 3·77 ; free fatty acids, 1·6 ; total fatty acids, 93·74 (mean molecular weight = 290) ; and unsaponifiable matter, 1·3 per cent.

Kryloff identified the presence of palmitic acid, and obtained di- and tetra-hydroxystearic acids, indicating the presence of oleic and linolic acids. The elaidin test also showed that the oil contained a small amount of olein.

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[1] *Zeit. angew. Chem.*, 1896, 581.

[2] *Chem. Centralbl.*, 1899, i., 592.

[3] *Chem. Zeit.*, 1900, xxxiv., 815.

[4] *Chem. Rev. Fett Ind.*, 1901, viii., 250.

Cedar-nut oil has weak drying properties, and, when boiled with manganese borate for four hours at 140° to 150° C., yields a product which dries to a firm film on glass in forty-eight hours.

According to *Glaesner*, it forms a red zone at the junction of the liquids when treated with an equal volume of concentrated hydrochloric acid.

CHERRY-LAUREL OIL.[1]

Recorded Values.

Cherry-Laurel Oil.

Specific gravity at 15° C.,	0·9230
Saponification value,	194
Iodine value,	108·9
Solidification point,	−19° to −20° C.
Maumené test,	44·5° C.
Melting point of fatty acids,	20° to 22° C.
Solidification point ,,	15° to 17° C.
Iodine value ,,	112·1

This oil is contained in the kernels of the cherry laurel, *Prunus cerasus*. It closely resembles cherry-kernel oil in its chemical and physical characteristics.

COTTON-SEED OIL.

Recorded Values.

Cotton-Seed Oil.

Specific Gravity.	Saponification Value.	Iodine Value.	Acetyl Value.	Refractive Index.	Authority.
0·923 -0·930	191-196·5	...	...	...	Allen.
0·9132-0·9154	...	109·0	...	...	Wiley.
0·9220	191·6-193·5	106·8-108·3	...	...	Thomson and Ballantyne.
...	...	...	...	1·4570 at 60° C.	Thoerner.
...	...	...	21·1-24·8	...	Lewkowitsch.
0·9230-0·9260(*a*)	192-194·5	112-116	...	...	Skukoff.
0·9230-0·9250	191-195	104-114	...	...	De Negri and Fabris.
...	...	...	...	Oleo-refractometer. +16 to +23	Pearmain.
...	...	...	...	+20	Jean.

(*a*) Samarkand oils.

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[1] De Negri and Fabris; Lewkowitsch, *Oils, Fats, and Waxes*, 352.

Fatty Acids.

Specific Gravity.	Melting Point.	Solidification Point.	Saponification Value.	Iodine Value.	Refractive Index.	Authority.
	°C.	°C.				
0·8467 at $\frac{99° \text{C.}}{15·5° \text{C.}}$	35·2	32	...	...	...	Allen.
0·8816 at $\frac{100° \text{C.}}{100° \text{C.}}$	...	...	...	...	...	Archbutt.
...	35-40	32-35	201·6	112-115	1·4460	Thoerner.
...	34-40	...	...	112 8-113	...	De Negri and Fabris.
		Dalican's Test.				
	...	32·2-35·2 (*a*)	...	...	...	Lewkowitsch.
...	...	35·6-37·6 (*b*)	...	...	...	,,
...	...	32-36 (*c*)	...	...	...	Shukoff.
				Liquid Acids.		
...	...	...	...	146 8-148·2	...	Wallenstein and Fink.
...	...	32·4-33·2	...	137·3-149·8	...	Lane.

(*a*) Part of "stearine" removed. (*b*) All "stearine" left. (*c*) Samarkand oils.

Source.—Cotton-seed oil is extracted or expressed from the seeds of different varieties of the cotton-tree, *Gossypium*, which is largely cultivated in Egypt and the United States.

The dark-coloured crude oil, obtained by the methods described in Chap. IX., is refined by treatment with a suitable proportion of alkali solution, which precipitates colouring matter and impurities (Chap. X.).

Composition.—*Schädler* gives the elementary composition of cotton-seed oil as:—Carbon, 76·40; hydrogen, 11·40; and oxygen, 12·20 per cent.

It consists mainly of glycerides of oleic and linolic acids, the relative proportions, according to Hazura, being as 3 : 4·5. The solid fatty acids are chiefly palmitic acid with a smaller quantity of stearic acid. *Farnsteiner* separated linolic tetrabromide from the total fatty acids in amount corresponding with 17 or 18 per cent. of linolic acid.

Oxidised acids are also said to be present in small quantity, one of them being "cotton-oleic acid," a higher homologue of ricinolic acid (*Papasogli*).

Properties and Tests of Purity.—Being generally refined with alkali, fresh cotton-seed oil usually contains but little, if any, free acid, and is, therefore, readily assimilated in cases of dyspepsia. It is of a pale yellow colour, and has a mild and pleasant taste.

Solidification Point.—Cotton-seed oil yields a deposit of the so-called "cotton-stearin" at about 12° C., and solidifies at 0° to − 1° C. A test for the detection of cotton-seed oil in olive oil (*q.v.*) has been based upon the lower solidification point of the latter.

Melting and Solidification Points of the Fatty Acids.—As a general rule, these are higher than those of most other oils, including olive oil. Tunisian olive oil, however, contains fatty acids, melting at similar high temperatures (34° to 37° C.).

Iodine Value.—In addition to the values given above, the following figures have been recorded:—102·5 to 106·4 (*Shermann* and *Snell*), 106 (*Hübl*), 108·76 Hübl value, 110 by Wijs' method (*Wijs*), 104 to 108 (*Oliveri*).

For the detection of cotton-seed oil in lard or olive oil, the determination of the iodine value of the "liquid" fatty acids gives more information than the iodine value. Thus *Wallenstein* and *Fink*[1] obtained the following results in this way:—

Oil.	Iodine Value of Liquid Acids.
Cotton-seed, . . .	146·8 to 148·2
Niger-seed, ...	147·5
Maize, ...	140·7
Earth-nut, ...	128·5
Rape, ...	120·7
Lard, European, . . .	95·2 to 96·6
,, American, . . .	104·5
Tallow, ...	92·2 to 92·7

Maumené Test.—The following figures have been given by different observers:—75° to 76° C. (*Maumené*), 74° to 75° (*Allen*), 80° to 90° (*Wiley*), 50° to 53° (*De Negri* and *Fabris*). Specific temperature reaction, 169° to 170° (*Thomson* and *Ballantyne*); halogen standard figure, 114·4 to 116·2 (*Mitchell*).

Drying Properties.—Cotton-seed oil possesses considerable drying capacity. In Bishop's test it absorbs about 9 per cent. of oxygen, whilst linseed oil absorbs about 17 per cent.

Colour Reactions—(1) **Nitric Acid Reaction.**—Equal volumes of the oil under examination and of nitric acid (sp. gr., 1·37) are shaken together and allowed to stand for twenty-four hours, a more or less pronounced brown coloration being obtained in the presence of cotton-seed oil. According to *Lewkowitsch*, this test is of great value, and is capable of detecting from 2 to 3 per cent. of cotton-seed oil in olive oil. The coloration is also given by cotton-seed oil after being heated to 240° C. Unfortunately a similar coloration is given by soya bean oil.

(2) **Becchi's Silver Nitrate Test.**—The reduction of silver nitrate as a test for cotton-seed oil, first proposed by Becchi, was subsequently recommended in a modified form by an Italian Official Commission.

According to *De Negri* and *Fabris*,[2] this modified test requires the following reagents:—

(i.) Silver nitrate, 1 gramme in 200 c.c. of 98 per cent. alcohol; ether, 40 c.c.; and nitric acid, 0·1 gramme.

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[1] *Chem. Zeit.*, 1895, xviii., 1189; *J. Soc. Chem. Ind.*, 1895, xiv., 78.

[2] *Zeit. anal. Chem.*, 1894, xxxiii., 560.

(ii.) Colza oil, 15 c.c. in amylic alcohol, 100 c.c.

The alcohol should be purified by repeated distillation with potassium hydroxide, whilst the colza oil should be cold-expressed oil filtered before use.

In applying the test, 10 c.c. of the oil under examination are mixed with 1 c.c. of reagent (i.), and then shaken with 10 c.c. of reagent (ii.), and divided into two parts, one of which is heated in boiling water for fifteen minutes, whilst the other is left in the cold. A reddish-brown coloration in the heated portion points to the presence of cotton-seed oil.

De Negri and *Fabris* obtained deeper colorations by heating the oil to 100° C. and then filtering it several times before applying the test. They also found that many specimens of pure olive oil gave a brown coloration, though not after being filtered while hot and allowed to stand at 100° C. for some hours.

According to *Becchi*, the use of colza oil is essential in testing old samples of cotton-seed oil. On the other hand, *Hehner*, *Bishop*, *Milliau*, and others omit the colza oil as unnecessary. *Hehner*, for instance, heats two parts of the oil with one part of the silver solution for fifteen minutes.

Milliau[1] prefers to apply the reduction test to the liberated fatty acids. 5 c.c. of the fatty acids are dissolved in 15 c.c. of 95 per cent. alcohol, heated to 90° C., then mixed with 2 c.c. of a 30 per cent. solution of silver nitrate, and the heating continued until a third of the alcohol has evaporated.

This modification, however, is not so sensitive as the original test (*Hehner*, *Lewkowitsch*).

Raikow and *Tscherweniawow*[2] find that the relative amount of silver nitrate present has a considerable influence on the degree of discoloration, whether or no the solution contains colza oil or nitric acid.

Of the different modifications of the test, they regard that prescribed by the Italian Commission as the most reliable. According to this modification, the silver nitrate solution must contain 0·04 per cent. of free nitric acid. With more the reagent is not sufficiently sensitive, whilst with less olive oil will give a reaction.

Soltsien[3] attributes the reaction in Becchi's test to the presence of a sulphur compound, and finds that it is strengthened by the presence of rape (colza) oil, which, however, after being heated to 150° C., no longer aids the reaction.

Charabot and *March*,[4] on heating cotton-seed oil fatty acids on the water-bath with silver nitrate and extracting the brown precipitate with petroleum spirit, obtained a dark brown residue consisting of silver sulphide and the silver salt of a fatty acid melting at 52° C. An analogous compound was isolated by *Dupont* and *Charabot*[5] from

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[1] *J. Soc. Chem. Ind.*, 1893, xii., 716.

[2] *Chem. Zeit.*, 1899, xxiii., 1025.

[3] *Chem. Centralbl.*, 1899, ii., 539.

[4] *Bull. Soc. Chim.*, 1899, xxi., 552.

[5] *Bull. Soc. Chim.*, xv., 341.

olive oil, and *Charabot* and *March* therefore consider that the silver nitrate test ought to be accepted with caution.

Raikow [1] invariably found chlorine compounds, but never sulphur, in cotton-seed oil.

Tortelli and *Ruggeri* [2] advocate the following modification of Becchi's test :—

Five grammes of the oil are saponified with 30 c.c. of an alcoholic solution of potassium hydroxide (60 grammes per litre), and the soap solution exactly neutralised and poured in a thin stream into a hot solution of lead acetate (50 c.c. of a 10 per cent. solution with 250 c.c. of water). The resulting lead soaps washed, dried on filter-paper, and heated with anhydrous ether for about twenty minutes under a reflux condenser. The ethereal solution is washed, the fatty acids liberated, the ether washed free from acid, evaporated, and the residue mixed with 10 c.c. of 90 per cent. alcohol and 1 c.c. of a 5 per cent. aqueous solution of silver nitrate, and warmed in water at 70° to 80° C.

In the case of pure olive oil, the liquid is stated to remain unaltered after thirty minutes, but a reduction is plainly visible within two minutes when as little as 1 per cent. of cotton-seed oil is present.

(3) **Halphen's Test.**[3]—From 1 to 3 c.c. of the oil is mixed with an equal volume of amylic alcohol and carbon bisulphide (containing about 1 per cent. of free sulphur), and the tube immersed in boiling brine for fifteen minutes. If no orange-red colour is produced, another 1 c.c. of carbon bisulphide is added. The coloration varies in intensity according to the origin and treatment of the cotton-seed oil, but in all cases of unheated oil is pronounced. By means of this test, *Halphen* was able to detect less than 5 per cent. of cotton-seed oil in other oils.

According to *Wauters*,[4] the reaction is also given by the fatty acids, though not after the latter have been dried at 100° C. The same chemist states that butter from cows fed on cotton-seed cake gives a coloration corresponding with about 1 per cent. of oil. Decolorisation of the oil or fat with animal charcoal renders the test more sensitive.

Raikow and *Tscherweniawow* [5] state that carbon bisulphide alone may give a coloration, but that the characteristic reaction is only obtained by the simultaneous action of carbon bisulphide and sulphur.

As in the case of Becchi's test, the sensitiveness of cotton-seed oil to Halphen's reagent is destroyed by heating it with superheated steam, or at 220° C.

Soltsien first advocated the disuse of amylic alcohol, but subsequently [6] concluded that the original test was the most reliable. He found that certain American lards gave a coloration equivalent to

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[1] *Chem. Zeit.*, 1899, xxiii., 769 and 802.

[2] *Chem. Zeit. Rep.*, 1898, xxii., 101.

[3] *J. Pharm. Chim.*, 1897, vi., 390.

[4] *Bull. de l'Ass. belge Chim.*, 1899, xiii., 404.

[5] *Chem. Zeit.*, 1899, xxiii., 1025.

[6] *Chem. Centralbl.*, 1901, i., 539.

about 1 per cent. of cotton-seed oil, this being possibly due to the food of the pigs.

Utz[1] finds that by using pentachlorethane instead of carbon bisulphide a higher temperature can be obtained, and the test rendered more sensitive, but as *Gastaldi* has found that an oil free from cotton-seed oil may give a red coloration when heated above 120° C., further tests are required before *Utz's* modification is accepted as trustworthy.

The value of Halphen's test is confirmed by *Wrampelmeyer*,[2] who has obtained unmistakable reactions with dark oils containing only 5 per cent. of cotton-seed oil.

According to the results of *Raikow's*[3] experiments, the active substances in Halphen's and Becchi's tests are not identical, as has been stated. The active agent in Halphen's test is rendered inert by being exposed to sunlight for a sufficient length of time.

Raikow[4] considers the active body to be an unsaturated acid, and draws an analogy between the reaction and the changes which aldehydic or ketonic compounds undergo under the influence of free sulphur, as in the case of valeric aldehyde.

$$\begin{aligned}(a)\quad 2C_5H_{10}O + S &= C_5H_{10}S + C_5H_{10}O_2.\\ (b)\quad C_5H_{10}S + 4S &= C_5H_6S_3 + 2H_2S.\end{aligned}$$

The liberation of hydrogen sulphide was observed during the course of Halphen's reaction. In Raikow's opinion the first part of the above reaction may correspond with the production of the red colour, and the second with its disappearance under the long-continued influence of sunlight.

Gastaldi[5] uses pyridine in place of amyl alcohol in the test, and is thus able to detect less than 0·5 per cent. of cotton-seed oil in olive oil.

As regards the temperature required to destroy the active agent, *Oilar*[6] finds that it lies between 315° and 320° C. when the cotton-seed oil is heated in glass vessels, but that, when iron vessels are used, the oil no longer gives the reaction after being heated to 140° to 150° C. The substance is apparently destroyed and not merely volatilised, since the fumes give no reaction.

Holde and *Pelgry*[7] had previously found that cotton-seed oil gave a fainter reaction after being heated at 200° to 210° C., and none at all after ten minutes at 250° C.

(4) **The Pentosan Test.**—*B. van Kettel*[8] based a test upon the fact that several vegetable oils, and notably cotton-seed oil, contain traces of pentosans, whilst animal fats are free from such compounds. Ten grammes of the oil are heated with a few c.c. of hydrochloric acid (sp. gr., 1·06), and a solution of phloroglucinol hydrochloride added after the layers have separated on standing for ten minutes, a red

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[1] *Chem. Rev. Fett Ind.*, 1913, xx., 291.

[2] *Zeit. Untersuch. Nahr. Genussm.*, 1901, iv., 25.

[3] *Chem. Zeit.*, 1900, xxiv., 562, 583.

[4] *Ibid.*, 1902, xxvi., 10.

[5] *J. Soc. Chem. Ind.*, 1912, xxxi., 934.

[6] *Amer. Chem. J.*, 1900, xxiv., 355.

[7] *Chem. Rev. Fett Ind.*, vi., 67 and 94.

[8] *Mon. Scient.*, 1900, xiv., 154.

ring being formed at the junction of the liquid when pentosans are present.

This reaction is said not to be given by cacao butter, earth-nut oil, croton oil, rape-seed oil, and linseed oil.

v. Kettel also obtained negative results with two specimens of pure olive oil. The reaction is greatly weakened or even destroyed by heating the oil at 250° C. It is capable of detecting from 10 to 5 per cent. of cotton-seed oil in earth-nut oil.

(5) **Cavalli's Test.**[1]—The oil is shaken with a mixture of 2 grammes of resorcinol, 20 c.c. of water, and 15 c.c. of sulphuric acid, a red coloration changing to blue being given by cotton-seed oil.

(6) **Hirschsohn's Gold Chloride Test.**—Five c.c. of the oil are heated for twenty minutes in boiling water with 5 or 6 drops of a solution of 1 gramme of crystalline gold chloride in 200 c.c. of chloroform, a red coloration being produced in the presence of cotton-seed oil.

From the results obtained by *Moerk*, *Holde*, and others, this reaction appears inconclusive, since it is given by several other oils, whilst, on the other hand, it is not given by heated cotton-seed oil.

Detection of Cotton-seed Oil in Animal Fats.—In addition to the preceding colour reactions, and the results of the various quantitative tests, the phytosterol tests (*q.v.*) will furnish corrobative evidence of the presence of cotton-seed oil in butter or in lard (see *Butter*, *Lard*). According to *Bömer*, the presence of 3 to 4 per cent. can be detected with certainty by this test.

Werenskiold[2] states that the butter of a cow fed daily upon 1 kilo. of cotton-seed meal gives the reactions for cotton-seed oil.

CROTON OIL.

Recorded Values.

Croton Oil.

Origin.	Specific Gravity at 15° C.	Hehner Value.	Saponification Value.	Iodine Value.	Acetyl Value.	Reichert-Meissl Value.	Authority.
...	0·9437	...	215·6	103·6-104·4	38·6	12·1	Dulière.
...	...	88·9	210·3-215·0	101·7-104·7	19·61-20	13·3-13·6	Lewkowitsch.
Expressed,	...	...	192·9	109	...	...	Javillier.
Extracted (ether),	...	...	194·5	108	...	...	,,
Extracted (alcohol),	...	...	260·6	91·2	...	...	,,
Commercial,	...	...	205·6	102	...	...	,,
Freshly expressed,	0·9426	...	...	...	...	...	Schädler.
Old, . . .	0·9550	...	...	...	...	...	,,

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[1] *Mon. Scient.*, 1900, xiv., 154.

[2] *J. Soc. Chem. Ind.*, 1899, xviii., 162.

Fatty Acids.

Solidification Point.	Iodine Value.	Authority.
16·4-16·7	111·2-111·7	Dulière.
18·6-19	...	Lewkowitsch.

Source.—Croton oil is obtained from the seeds of *Croton tiglium*, a plant cultivated in Southern Asia and China, and on the Malabar Coast.

The commercial oil is stated by *Javillier* to be frequently prepared by expression, followed by digestion with alcohol of 80 per cent. strength.

Composition.—According to *Schädler*,[1] it contains the glycerides of stearic, palmitic, myristic, lauric, caproic, butyric, and acetic acids, with the glycerides of tiglic acid and higher homologues of oleic acid, but not olein itself.

Dunstan and *Boole* [2] isolated a resinous constituent to which they attributed the vesicating action of croton oil, by fractionally precipitating the lead salts with water from an alcoholic solution. This substance, which melted at 90° C., had an empirical composition, $C_{13}H_{18}O_4$, and was apparently of a lactonic nature.

Properties.—When hydrogenated croton oil loses its physiological properties.[3] The great discrepancies in the recorded values of croton oil are attributed by *Javillier* [4] to the different methods of obtaining the oil. Thus the expressed oil differs considerably from the extracted oils in the cases in the above table, particularly from that extracted with alcohol.

On the other hand, *Dulière* [5] asserts that the cold-drawn oil differs from the oil obtained by hot expression in colour, solubility in absolute alcohol, and acidity, but is the same in other respects.

Solidification Point.—*Schädler* gives the solidification point as − 18° C., whilst the figures given by *Javillier* vary from − 7° to −8° C.

Acidity.—*Dulière* found the acid value (*Burstyn*) to be 21·8, whilst in *Javillier's* samples it ranged from 27 in the expressed oil to 60·1 in the oil extracted with alcohol.

Drying Properties.—Croton oil has weak drying properties.

Elaidin Reaction.—No solid product is formed.

Solubility.—The expressed oil and that extracted with ether are soluble in 2 parts of absolute alcohol at 75° C., whilst the oil extracted by means of alcohol dissolves at the ordinary temperature.

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[1] *Technologie der Fette*, 545.

[2] *Proc. Roy. Soc.*, 1893, lviii., 238.

[3] *Ber.*, 1909, xlii., 1546.

[4] *J. Pharm. Chim.*, 1898, vii., 524.

[5] *Ibid.*, 1899, x., 305.

It is also soluble in petroleum spirit, which fact affords an easy means of distinguishing between croton and castor oils.

Specific Gravity.—According to *Schädler*, the specific gravity increases on keeping. Thus the density of an oil rose from 0·9426 to 0·9550.

Refractometer.—The following results were obtained by *Dulière*:—Butyro-refractometer, 77·5 at 27° C.; oleo-refractometer, + 35 at 22° C.

Detection of Adulteration.—*Hydrocarbons*, which are sometimes added, can be detected by distillation in a current of steam, and their amount calculated from the saponification value.

Castor Oil can be detected by the difference in solubility and the acetyl value.

Maupy[1] tests for castor oil by heating about 10 grammes of the oil with potassium hydroxide in a silver basin, and noting whether any odour of caprylic alcohol results, and whether crystals of sebacic acid are obtained when the residue is boiled with water.

GARDEN CRESS OIL.

Recorded Values.

Garden Cress Oil.

Specific Gravity.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Refraction at 40° C.		Solidification Point.	Authority.
						Scale Divisions.	Refractive Index.		
At 15° C. 0·924	...	...	...	...	...	...	...	°C. − 15	Schädler.
0·920	...	178	108 to 108·8	...	...	...	...	...	De Negri & Fabris.
At 15·5° C. 0·9210	10·55	181·5	101·72	0·44	...	60·5	1·4622	...	Crossley & Le Sueur.
0·9211	4·18	183·1	118·4	0·22	95·57	...	...	..	,,

This oil is obtained from the seeds of the garden cress, *Lepidium sativum*.

It belongs to the class of semi-drying oils.

Specimens of the oil examined by *De Negri* and *Fabris* gave Maumené figures of 92° to 95° C.

The viscosity was found by *Crossley* and *Le Sueur*[2] to be 12·66, compared with water at 70° F. as unity.

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[1] *J. Pharm. Chim.*, 1894, iii., 362.

[2] *J. Soc. Chem. Ind.*, 1898, xvii., 992.

HICKORY-NUT OIL.

Recorded Values.

Hickory-Nut Oil.

Specific Gravity.	Iodine Value.	Heat of Combustion. Calories per Gramme.	Refractive Index at 20° C.	Authority.
0·9164 at 24° C.	102·79	9450	1·4696	Merrill.

This oil is contained in the nuts of the hickory trees, *Carya alba* and *C. porcina*.

KAPOK OIL.

Recorded Values.

Kapok Oil.

Specific Gravity at 18° C.	Saponification Value.	Hehner Value.	Iodine Value.	Maumené Test.	Authority.
				° C.	
0 9199	181	94·9	116	95	Henriques.[1]

Fatty Acids.

Specific Gravity at 18° C.	Melting Point.	Solidification Point.	Saponification Value.	Mean Molecular Equivalent.	Iodine Value.	Authority.
	° C.	° C.				
0·9162	29	23-24	191	293	108	Henriques.

This oil is expressed from the seeds of the kapok tree (*Eriodendron anfractosum*, L.), which is cultivated in the Dutch East Indies. It belongs to the natural order *Malvaceæ*, but resembles the cotton-plant (*Gossypium*) in possessing a similar fibrous covering to its seeds. This cotton-like material is used as stuffing for beds, etc., but is unsuitable for textile purposes. An oil with closely similar characteristics is obtained from *Bombax malabaricum*.

Sprinkmeyer and *Diedrichs*[2] obtained the following results with kapok oil derived from different species of these plants :—

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[1] *Chem. Zeit.*, 1893, xvii., 1283.

[2] *Zeit. Unters. Nahr. Genussm.*, 1913, xxvi., 86, 450.

Source.	Java, E. Africa, etc.	B. malabaricum.	Mexican Bombax.	Commercial Oil.
Sp. gr. at 15°/15° C. (Zeiss)	0·9235-0·9326	0·9600	..	0·9217
Ref. ind. at 40° C., .	51·7-59·7	57·0	57·4	56·2
Iodine value, . .	85·2-93·5	73·6	95·7	97·54
Acid value, . . .	18·5-21·02	3·0	12·62	15·0
Saponification value, .	189·2-194·5	194·3	192·8	192·5

The expressed oil (about 40 per cent. of the kernels) is used in Holland as food and in the manufacture of soap. It is greenish-yellow in colour and has a slight odour. On standing, it deposits stearine in like manner to cotton-seed oil, which it also resembles in other respects, though it dries somewhat more rapidly.[1]

When treated with nitric acid it gives a coloration similar to that given by cotton-seed oil, though not so rapidly, and it also gives a slight reaction in Halphen's test. It may be distinguished from cotton-seed oil by the following modification of Becchi's test, due to *Durand* and *Band*:—Fifteen c.c. of the oil are saponified, the soap dissolved in 200 c.c. of water, the alcohol evaporated, and the fatty acids liberated with a slight excess of N-sulphuric acid. The cake of acids is shaken twice with 15 c.c. of *cold* water, and dried in the oven at 105° C. Five c.c. of these acids are shaken with 5 c.c. of a 1 per cent. solution of silver nitrate in absolute alcohol. In the case of cotton-seed oil only a faint brown coloration is obtained, whilst kapok oil gives a deep coffee-brown coloration. By means of this test 1 per cent. of kapok oil can be detected in other oils.

OIL OF LUFFA ÆGYPTICA.

Recorded Values.

Oil of Luffa Ægyptica.

Specific Gravity at 15·5° C.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Refraction at 40° C.		Authority.
						Scale Divisions.	Refractive Index.	
0·9254	28·85	187·8	108·5	1·43	94·8	62·0	1·4660	Crossley and Le Sueur.

This specimen of oil examined by *Crossley* and *Le Sueur* was derived from the seeds of *Luffa œgyptica*, climbing plants belonging to the *Cucurbitaceœ*.

The oil was reddish-brown in colour and had a slight odour. It

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[1] Crossley and Le Sueur, *J. Soc. Chem. Ind.*, 1898, xvii., 992.

belongs to the class of semi-drying oils. It is used by the natives of India for medicinal purposes.

MADIA OIL.

MADIAOEL.

Recorded Values.

Oil.

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Maumené Test.	Solidification Point.	Authority.
			° C.	° C.	
0·9230-0·9286	93	121	95-99	− 10 to − 20	De Negri and Fabris.
0·9286	...	...	...	− 10 to − 11	Schädler.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
° C. 23-26	° C. 20-22	120·7	De Negri and Fabris.

This oil is obtained from seeds of *Madia sativa*, a plant indigenous to Chili. It contains palmitin, stearin, olein, and probably linolin. The cold-drawn oil is used as an edible oil, whilst that obtained by hot expression is employed in the manufacture of soap and for burning and lubricating purposes. It is dark yellow in colour.

According to *De Negri* and *Fabris*,[1] it is usually purified with sulphuric acid, which has the effect of rendering it more liquid.

In the elaidin reaction it yields a fluid mass. It gives a very slight brown coloration in Becchi's test.

Schädler states that it is soluble in thirty times its volume of cold and six times its volume of hot alcohol.

Source.—Maize oil is expressed or extracted from the seed of the maize plant *Zea mais*, in which it is present to the extent of 6 to 8 per cent.

Uses.—It is used as a salad oil, and for soap-making and burning, but, owing to its drying properties, it is unsuitable for lubricating purposes.

It is also employed in the manufacture of margarine in the place of cotton-seed or sesamé oil, and a few years ago was used to a considerable extent to adulterate lard.

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[1] *Zeit. anal. Chem.*, 1894, xxxiii., 564.

MAIZE OIL.

CORN OIL, HUILE DE MAIS, MAISOEL.

Recorded Values.

Oil.

Specific Gravity.	Hehner Value.	Saponification Value.	Reichert Value.	Iodine Value.	Refractive Index.	Acetyl Value.	Unsaponifiable Matter.	Authority.
							Per cent.	
0·9215-0·9244	...	188-193	...	111-123	...	...	...	De Negri and Fabris.[1]
0·9245-0·9262	93·57	...	...	121·5-123·1	...	...	2·86	Hopkins.[2]
0·9244-0·9268 at 15·5° C.	...	186·2-190·1	...	120·8-127·4 (*Hübl*) 122·2-128 (*Wijs*)	...	...	1·46-1·71	Williams.[3]
0·9243	...	189·7	...	122·7	...	...	1·69	Archbutt.[4]
...	...	...	4·2-4·3	...	...	11·12-11·42	2·52	Vulté and Gibson.[5]
...	...	...	...	...	...	7·8 - 8·75	...	Lewkowitsch.
(I.) 0·9213 at 15·5° C.	92·23	192·6	4·2	118·62	1·4766	11·1	1·43	Winfield.
(II.) 0·9213 ,,	92·79	192·6	4·3	119·74	1·4761	11·49	1·39	,,
(III.) 0·9255 ,,	88·21	191·7	9·9	113·27	1·4765	...	...	,,
(IV.) 0·9234	...	189·5	...	112·76	1·4766	12·5	...	,,

(I.) Expressed oil. (II.) Expressed oil, 10 years old. (III.) Distillery oil, 15 years old. (IV.) Steamed oil.

Fatty Acids.

Specific Gravity.	Melting Point.	Solidification Point.	Iodine Value.	Saponification Value.	Authority.
	°C.	°C.			
...	17-20	16-14	113-115	...	De Negri and Fabris.
...	17	...	126·4	...	Hopkins.
0·8529 at 100° C.	22·4	...	120·98	198·3	Winfield.
...	...	...	Liquid Acids. 140·7	...	Wallenstein and Fink.

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[1] *Zeit. anal. Chem.*, 1894, xxxiii., 565.

[2] *J. Amer. Chem. Soc.*, 1898, xx., 948.

[3] *Analyst*, 1899, xxv., 146 (8 samples of oil).

[4] *J. Soc. Chem. Ind.*, 1898, xviii., 346.

[5] *J. Amer. Chem. Soc.*, 1901, xxiii.. 1.

Composition.—The following fatty acids have been identified in maize oil:—Oleic, linolic, stearic, palmitic, arachidic (*Vulté* and *Gibson*), hypogæic (*Vulté* and *Gibson*), and ricinoleic acids (*Rokitiansky*).

Hopkins obtained from a specimen of the oil 93·6 per cent. of insoluble fatty acids, consisting of about 4·5 per cent. of saturated fatty acid, 44·8 per cent. of olein, and 48·2 per cent. of linolin. The oil also contained 1·37 per cent. of phytosterol and 1·49 per cent. of lecithin.

Vulté and *Gibson* (*loc. cit.*) found the proportion of glycerol to vary from 10·35 to 10·55 per cent., whilst the phytosterol amounted to 1·41 per cent. and the lecithin to 1·11 per cent. The solid and liquid fatty acids, separated by treatment of the lead salts with ether, were respectively 27·74 and 72·26 per cent. Among the soluble fatty acids, formic and acetic acids were identified, whilst caproic, caprylic, and capric acids had previously been found by *Rokitiansky* in maize oil.

Hehner and *Mitchell*[1] did not obtain any deposit of stearic acid from the mixed fatty acids of maize oil.

Properties and Tests of Purity.—Maize oil has the odour and flavour of the grain. When freshly extracted it is nearly colourless, but gradually changes to pale straw colour and finally to golden yellow under the influence of atmospheric oxidation.

The oil extracted from the dried grains from a brewer's mash is much darker in colour. The characteristics of such an oil are shown in the Table of Values (No. III.).

Solidification Point.—Maize oil solidifies at − 10° to − 12° C. according to *De Negri* and *Fabris*, and at − 36° C. according to *Hopkins*.

Free Fatty Acids.—The percentage of free fatty acid (as oleic acid) found by *Williams* in eight samples of oil ranged from 1·50 to 3·64. *Archbutt* found another sample to contain 2·4 per cent. A crude oil examined by *Sherman* and *Snell* contained 1·68 per cent., and two refined oils 2·56 and 3·32 per cent. of free acids. In a sample of freshly expressed oil *Winfield* found free acids corresponding with an acid value of 2·25, whilst in old oils the values were 3·70 (II.) and 20·65 (III.).

Iodine and Bromine Values.—The following additional iodine values have been recorded:—122·9 (*Smith*), 125 (*Spüller*), 120·3 to 122·4 (*Sherman* and *Snell*).

Williams (*loc. cit.*), in a series of comparative determinations, obtained bromine values about 2 per cent. lower than the bromine values calculated from the iodine values.

The bromine thermal value is slightly too low when compared with the results given by almond oil. Thus *Hehner* and *Mitchell*[2] obtained a bromine thermal value of 21·5, which gave a calculated iodine value of 118·2, as against 122 by Hübl's process. *Vulté* and *Gibson* obtained a bromine thermal value of 21·6.

Maumené Test.—The following figures are recorded:—84 to 89 (*De Negri* and *Fabris*), 81·6 (*Archbutt*), 74 to 77 (*Winfield*). Specific

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[1] *Analyst*, 1896, xxi., 328.

[2] *Analyst*, 1895, xx., 149.

temperature reaction, 176·2 to 178·6 (*Winfield*). *Mitchell*[1] has shown that the Maumené figure of fresh unoxidised oil is proportional to the bromine thermal value. The *halogen standard figure* with sulphuric acid of 93·8 per cent. strength was 19·2 to 19·4.

Drying Properties.—Maize oil has weak drying properties, and when heated for a few days forms a solid film. *Williams* found the maximum increase in weight of a film of maize oil to be 1·5 per cent., as compared with an increase of weight of at least 4 per cent. shown by good linseed oil. In Williams' opinion, the oil is unlikely to be of much service for paints or varnishes.

When "blown" at 150° C., maize oil thickens, though to a less extent than cotton-seed oil. *Archbutt*, however, states that it readily yielded an excellent blown oil.

In another place, *Archbutt* (*loc. cit.*) gives the following results obtained by exposing thin films of different oils to the atmosphere at a temperature of 50° C. :—

Oil.	Time of Drying 0·1 Gramme of Oil on Glass.
Olive, ...	More than 3 days.
Rape, ...	About 48 hours.
Curcas, ...	24 to 30 ,,
Cotton-seed, ...	21 ,,
Maize, ...	18 ,,
Linseed, ...	12 ,,

By Livache's test, *Winfield* found two samples of expressed oil to gain 5·19 and 5·97 per cent. in weight in ten and seven days respectively, whilst oil steamed by his method (*vide infra*) gained 3·5 per cent. in four days.

Viscosity.—*Archbutt* found a specimen of maize oil to have a somewhat lower absolute viscosity than cotton-seed oil, 0·789 as against 0·82 to 0·91.

Winfield gives the viscosity of three oils (I., II., IV. in table) as 10·27, 9·79, and 10·70, compared with water at 20° C.; and 73·89, 70·42, and 76·50, compared with rape oil at the same temperature.

Elaidin Test.—Maize oil yields a yellow semi-solid mass after twenty-four hours, which eventually separates into yellow deposit and red supernatant liquid.

Detection of Adulteration.—The presence of *cotton-seed oil* in maize oil will be indicated by the increase in the melting point of the fatty acids, the lower acetyl value, and by Halphen's colour reaction.

Mineral or *rosin oils*, which are sometimes added, will be shown by the amount of unsaponifiable matter, considered in conjunction with the chemical and physical constants.

For the detection of *maize oil* in *butter* or *lard*, the phytosterol test, iodine value, and determination of linolic tetrabromide formed on bromination will be of service.

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[1] *Analyst*, 1901, xxvi., 174.

Steam Treatment of Maize Oil.—*Winfield*[1] describes a process of improving the oil for commercial purposes. The freshly-expressed oil is distilled with steam for eight hours, sufficient heat to prevent condensation being applied beneath the retort. This causes considerable dissociation of lower esters, and a large amount of an insoluble fatty acid collects in the retort and receiver. The residual oil is separated from the water in the retort, repeatedly washed with boiling water, dried, and filtered.

Oil thus treated is said to be lighter in colour and to have increased drying properties and less acidity, thus being more suitable for food and for use as a medium for paints.

The alteration in the chemical characteristics is shown in the table of recorded values (*supra*), where the steamed oil (IV.) was prepared from the expressed oil (I.).

PUMPKIN-SEED OIL.

Recorded Values.

Pumpkin-Seed Oil.

Origin.	Specific Gravity.	Acid Value.	Saponification Value.	Iodine Value.	Solidification Point.	Melting Point of Fatty Acids.	Solidification Point of Fatty Acids.	Authority.
	15° C.				° C.	° C.	° C.	
...	...	...	...	121	...	...	...	Hübl.
Expressed,	0·9231	...	188·1	...	– 15	28	24·5	Schädler.
Extracted with acetone	0·9208	18·9	192·5	...	...	..	...	Graham.
Commercial,	0·9197	3·5	195·2	...	...	...	...	,,
I. Cold expression	.	...	189·3 to 189·5	124·5	...	...	...	Poda.[2]
I. Hot expression	...	...	189·3 to 189·4	123·7	...	..	...	,,
II. Cold expression	..	..	189·9	125·1	.	...	...	,,
II. Hot expression	...	...	139·6	124·3	...	.	...	,,
Commercial (10 samples),	0·923 to 0·925	...	188·4 to 190·2	122·76 to 130·7	...	26·5 to 28·5	...	,,

Pumpkin-seed oil is obtained by expression or extraction from the decorticated seeds of *Cucurbita pepo*. It is largely used as an edible oil and for illuminating purposes, particularly in Austria and Hungary, whilst the oil extracted with ether is also employed as a vermifuge.

Poda states that in Austria-Hungary it ranks next to olive oil in price.

The oil obtained by cold expression is viscous and of a brownish-green colour, that extracted by means of solvents being of a redder colour.

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[1] *Investigation of Maize Oil*, Pamphlet, New York, 1899.

[2] *Zeit. Untersuch. Nahr. Genussm.*, 1898, i., 625.

Poda states that cold expression is the ordinary manufacturing process, whilst *Graham*[1] asserts that most of the oil of commerce is extracted by means of solvents, and that expressed oil is rare and considerably dearer. In Graham's opinion, the differences in the chemical and physical characteristics of different samples must be attributed to the difference in the method of obtaining the oil.

Pumpkin-seed oil is readily soluble in ether, carbon bisulphide, and in twenty times its volume of absolute alcohol.

It possesses considerable drying powers, and, when exposed to the air for some time, forms a yellow transparent mass.

It has a high viscosity, though not so great as that of olive oil.

In the elaidin test, it becomes slightly thicker after twenty-four to twenty-eight hours, whilst the colour changes to dark reddish-brown.

Poda (*loc. cit.*) obtained butyro-refractometer readings of 70·0 to 72·5 with fourteen different samples of the oil.

The oils principally used for adulterating pumpkin-seed oil are linseed, sesamé, cotton-seed, and rape oils. Any addition of these oils will be indicated by variations in the iodine value, specific gravity, refractometer reading, and melting point of the fatty acids.

Since the oil gives no coloration with Becchi's or Baudouin's tests, these tests can also be used to detect adulteration.

SESAMÉ OIL.

GINGELLY OIL.

Recorded Values.

Sesamé Oil.

Origin.	Specific Gravity.	Reichert-Meissl Value.	Saponification Value.	Iodine Value.	Refractive Index.	Authority.
...	0·9210-0·9237	...	188·5-190·4	106·9 to 107·8	1·4568 at 20° C.	De Negri & Fabris.
...	...	1·2	192-193	103-105	1·4561	Thoerner.
					Refractometer at 25° C.	
African, .	0·9232 at 15°C.	...	...	106·3	67·5	Utz.
Indian, .	0·9218 ,,	...	...	104·8	66·2	,,
Levantine,	0·922 ,,	...	...	107·7	67·0	,,
Russian, .	0·924-0·926 ,,	...	188-190	114-115	...	Shukoff.
Commercial,	0·9235	...	192-193	103-105	...	Schädler.
					Oleo-refractometer at 22° C.	
...	...	...	...	...	+12 to +17	Pearmain.
...	...	...	189·2	...	...	Lane.

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[1] *Chem. Rev. Fett Ind.*, 1901, viii., 187.

Fatty Acids.

Origin.	Saponification Value.	Melting Point.	Solidification Point.	Iodine Value.	Refractive Index.	Authority.
		° C.	° C.			
...	201·6	24-26	20-22	111·8-112	...	De Negri and Fabris.
. .	...	25-32	23·5	110-111	1·4461	Thoerner.
					Oleo-refractometer at 25° C.	
African, .	...	24·6-24·8	...	...	53·2	Utz.
Indian, .	...	24·2-24·8	...	...	53·5	,,
Levantine,	...	24·6-24·7	...	...	54·0	,,
Russian, .	...	...	23·4	...	...	Shukoff.
Commercial,	...	35-36	31·5-32	110-111	...	Schädler.
			Dalican's Test.			
...	...	...	21·2-23·8	...	...	Lewkowitsch.
				Of Liquid Fatty Acids.		
...	...	...	21·4	139·9	...	Lane

Source.—Sesamé oil is obtained from the seeds of white sesamé, *Sesamum orientale*. It was used as an edible oil in Ancient Egypt and Babylonia, and is now cultivated in most eastern and tropical countries, India, South Africa, and the Southern States of North America.

The oil is obtained by pressure, the two first pressings in the cold, and the last hot. According to *Schädler* the total yield is 45 to 50 per cent., comprising 25 to 30 per cent. of the finest table oil, 10 per cent. of fine edible oil, and 10 per cent. of ordinary oil. It is also used for illuminating and lubricating purposes, and in the manufacture of soap.

Indian sesamé oil (" tel " oil) is used in the manufacture of perfumes, soap, and margarine. It can be bleached by treatment with animal charcoal and French chalk, whilst caustic soda both bleaches and deodorises the oil, but the colour slowly returns.[1]

Composition.—The elementary composition of the oil is given by *Schädler* as—Carbon, 75·22; hydrogen, 11·13; and oxygen, 13·65 per cent.

It consists essentially of glycerides of oleic and linolic acids, with smaller quantities of stearin, palmitin, and myristin.

Farnsteiner[2] found a specimen of the oil to contain 12·1 per cent. of solid fatty acids, and about 16 per cent. of linolic acid. A second specimen extracted in the laboratory gave the following results:—Solid acids, 14·1; liquid acids, 86·7; and linolic acid, 12·6 per cent.

Lane[3] obtained 78·05 per cent. of liquid fatty acids (iodine value 139·9) from a specimen of sesamé oil.

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[1] Rai and Dunnicliff, *J. Soc. Chem. Ind.*, 1919, xxxviii., 99 R.

[2] *Zeit. Untersuch. Nahr. Genussm.*, 1899, ii., 1.

[3] *J. Soc. Chem Ind.*, 1901, xx., 1083.

Villavecchia and *Fabris*,[1] by extracting the barium soap of the oil with boiling alcohol, obtained an extract from which they isolated :—

1. An alcohol, $C_{25}H_{44}O$, melting at 137° C., and having a specific rotation $[\alpha]_D = -34° 23'$ at 20° C.

2. A crystalline substance, *sesamin*, melting at 123° C., and having $[\alpha]_D = +68° 36'$.

3. A viscid oil to which they attributed the coloration produced in Baudouin's test (*vide infra*).

Bömer [2] distinguishes between sesamin and phytosterol by testing the dried substance under the microscope with a mixture of sulphuric acid and acetic anhydride (as a diluting agent) in equal parts. Sesamin changes in colour from brownish-green to reddish-blue, and alters in shape, whilst phytosterol crystals do not alter either in colour or form. Pure sesamin melts at 120° to 122° C., and is dextro-rotatory. It is present in sesamé oil to the extent of 0·2 to 0·5 per cent.

The red oil (*Villavecchia* and *Fabris*) in the mother-liquor from the phytosterol and sesamin can be extracted by treatment with animal charcoal and extraction of the deposit with ether. It reacts with furfural and hydrochloric acid in a solution containing 1 part in 500,000.

Treatment with animal charcoal will also remove this active constituent from sesamé oil, and the oil can also be rendered inactive by heating it for some days on the water-bath.

Properties and Tests of Purity.—Sesamé oil is pale yellow in colour, and has a pleasant grain-like odour.

Solidification Point.—*De Negri* and *Fabris* give the solidification point of sesamé oil as − 4° to − 6°, whilst *Schädler* gives − 5° C.

Optical Activity.—Sesamé oil rotates the beam of polarised light to the right. Thus *Utz* [3] obtained the following readings in a 200 mm. tube at 15° C. :—African oil, + 1·6 ; Indian oil, + 1·4 ; and Levantine oil, + 0·8. In the absence of croton or castor oil, this characteristic may afford information as to the purity of sesamé oil.

Elaidin Test.—Sesamé oil yields a reddish-brown semi-solid mass after twenty-four hours.

Drying Properties.—Sesamé oil is inferior to cotton-seed oil as a drying oil. Thus *Fahrion* found that in Livache's test the maximum increase in weight was 3·6 per cent., as compared with 5·6 per cent. for cotton-seed oil.

Maumené Test.—The following figures have been recorded :—*Maumené*, 68° ; *Archbutt*, 65° ; *De Negri* and *Fabris*, 63° to 64°. *Mitchell* found that the "halogen standard figure" was proportional to the iodine value (see Chap. VII.).

Bromine Thermal Value.—This agrees well with the iodine value as determined by Hübl's or Wijs' method.

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[1] *J. Soc. Chem. Ind.*, 1894, xiii., 69.

[2] *Zeit. Untersuch. Nahr. Genussm.*, 1899, ii., 705.

[3] *Chem. Centralbl.*, 1900, ii., 293.

Colour Reactions.—The most characteristic test for sesamé oil, and one of the most reliable tests in oil analysis, is what is commonly known as *Baudouin's test.*

Baudouin's Test.—This test, originally devised by *Camoin*, consists in shaking 20 c.c. of the oil with 10 c.c. of hydrochloric acid of specific gravity 1·19, containing 0·1 gramme of cane sugar in solution, and allowing the mixture to stand, when a crimson colour is obtained in the presence of sesamé oil.

Use of Furfural.—*Villavecchia* and *Fabris*[1] found that the colour was due to the furfural formed by the action of the hydrochloric acid upon the sugar, and recommended the use of the following reagent in preference to the acid solution of cane sugar:—10 c.c. of the oil are mixed with a 0·1 c.c. of solution of 2 grammes of furfural in 100 c.c. of alcohol, and 10 c.c. of hydrochloric acid (specific gravity, 1·19) added. The tube is shaken for half a minute and allowed to stand, a red colour being obtained in the presence of as little as 1 per cent. of sesamé oil.

Kerp[2] obtains a clear colourless solution of furfural by twice distilling the commercial substance under reduced pressure. This purified furfural is very stable in a 1 per cent. alcoholic solution.

Colourless furfural is soluble in fuming hydrochloric acid, but the solution speedily changes to violet, then wine-red, and finally deposits a black precipitate. According to Kerp, however, no mistake can occur in testing sesamé oil with acid of specific gravity 1·16, provided that not more than 0·1 to 0·2 of a 0·99 per cent. alcoholic solution of furfural be used.

Kerp also found that it was possible to detect sesamé oil in a 0·2 per cent. solution by this test, and concluded that in practice 2 to 2·5 grammes of sesamé oil, corresponding to 20 to 25 grammes of margarine (containing 10 per cent. of sesamé oil), could be detected in a kilo. of butter.

In his opinion, the active constituent of the sesamé oil combines with the furfural to form a compound which unites with the acid, forming a red substance, which is decomposed on the addition of water, forming a thick orange-coloured liquid, whilst the acid is set free.

Soltsien[3] distinguishes between the colorations given in the Baudouin test, and by furfural and hydrochloric acid alone, by the differences in the respective spectra.

The reaction is not given by old rancid fats containing sesamé oil, and when fresh sesamé oil is added to the mixture the Baudouin coloration gradually becomes weaker, and finally ceases to be produced (*Soltsien*[4]).

Behaviour of Old Sesamé Oil.—Baudouin's test sometimes gives a blue coloration with old specimens of sesamé oil (*Ambühl*). This has

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[1] *J. Soc. Chem. Ind.*, 1894, xiii., 69.

[2] *Zeit. Untersuch. Nahr. Genussm.*, 1899, ii., 473.

[3] *Chem. Centralbl.*, 1899, i., 68.

[4] *Ibid.*, 1899, ii., 505.

been shown by *Kreis*[1] to be due to a mixture of the red colour of the ordinary furfural reaction with the green colour produced by treating old sesamé oil with hydrochloric acid of specific gravity 1·19 (*Bishop's reaction, vide infra*). The blue colour is best obtained by the use of sugar instead of furfural.

Sensitiveness of the Reaction.—*Villavecchia* and *Fabris* were able to detect 1 per cent. of sesamé oil in other oils by the Baudouin test. *Utz*[2] finds the limit of the test to lie between 0·5 and 1 per cent. He agrees with Soltsien's conclusion that the intensity of the coloration stands in some relationship to the colour of the seeds whence the oil was extracted. According to *Ranwez*,[3] the smallest amount of sesamé oil capable of detection in olive oil is between $\frac{1}{500}$ and $\frac{1}{1000}$ per cent.

Action of Heat on the Active Substance.—According to *Tortelli* and *Ruggeri*,[4] the active agent in sesamé oil is not destroyed by heating the oil for ten to twenty minutes at 200° to 250° C.

Behaviour of certain Olive Oils in the Baudouin Test.—*Villavecchia* and *Fabris* found that certain varieties of olive oil gave a coloration in Baudouin's test resembling that given by oil containing a small proportion of sesamé oil. The same observation was made by *Domergue* with reference to Tunisian and Algerian oils, and by *da Silva* in the case of Portuguese olive oils. In each case the fatty acids were found to give a negative result in the test. (See *Olive oil.*)

In such doubtful cases Tambon's and Tocher's reagents (*vide infra*) may be of service.

Tambon's Reagent.—*Tambon*[5] recommends the use of a reagent prepared by dissolving 4 grammes of crystalline glucose in 100 c.c. of hydrochloric acid, about 4 c.c. being added to 8 c.c. of the oil. The coloration given by sesamé oil is stated to be more stable than the colour of Baudouin's test, remaining unchanged for two to three weeks. A further advantage is that the reaction is not obtained with certain olive oils which give a coloration with cane sugar or furfural and hydrochloric acid.

Soltsien[6] finds that Tambon's reagent is not capable of detecting less than 2 per cent. of sesamé oil, and is thus less sensitive than Baudouin's reagent.

Bishop's Reaction.[7]—When sesamé oil that has been exposed to the action of light and air for some days is shaken with $1\frac{1}{2}$ times its volume of hydrochloric acid (sp. gr. 1·19) and allowed to stand, the acid layer is coloured green, the amount of coloration depending upon the age of the oil.

Utz (*loc. cit.*) found that the strongest green coloration was given by Indian oil, and the weakest by Levantine oil. He was able to detect from 5 to 10 per cent. of sesamé oil by that test in other oils.

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[1] *Chem. Zeit.*, 1899, xxiii., 802.

[2] *Chem. Centralbl.*, 1900, ii., 293.

[3] *Ibid.*, 1901, ii., 1240.

[4] *Zeit. Untersuch. Nahr. Genussm.*, 1901, iv., 161.

[5] *J. Pharm. Chim.*, 1901, xiii., 57.

[6] *Chem. Rev. Fett Ind.*, 1901, viii., 202.

[7] *J. Soc. Chem. Ind.*, 1890, ix., 112.

Kreis (*loc. cit.*) attributes the green coloration in Bishop's reaction to the presence of oxidation products of the glycerol, and suggests that the reaction may be used to detect rancidity in a fat. Thus he found that old butter, lard, and olive oil, which by themselves gave no coloration with hydrochloric acid, gave the green coloration when mixed with fresh sesamé oil.

Tocher's Reaction.[1]—Fifteen c.c. of the oil are shaken with an equal amount of a solution of 2 grammes of pyrogallol in 30 c.c. of hydrochloric acid. After standing for some time, the oily layer is decanted, and the hydrochloric acid heated for five minutes. In the presence of sesamé oil a reddish-purple colour is produced.

According to *da Silva*,[2] this test gives negative results with those varieties of olive oil (Portuguese) that give a coloration with Baudouin's test. The value of the reagent in this respect is also confirmed by *Bellier*.[3]

Formaldehyde Test.[4]—On shaking sesamé oil with an equal volume of a mixture of sulphuric acid (100 c.c.), water (50 c.c.), and 40 per cent. formaldehyde solution (10 c.c.), a dark blue colour is obtained.

In the case of olive, earth-nut, cotton-seed, poppy, walnut, and linseed oils, a yellow coloration is produced, whilst with mixtures containing sesamé oil the emulsion is dark grey to black, and the acid layer that separates dark brown to bluish-black. According to *Bellier*, the test is capable of detecting 1 per cent. of sesamé oil in other oils, even in Tunisian olive oils that give a coloration in Baudouin's test.

Breinl's Reaction.—In this test 10 c.c. of the oil are shaken with 0·1 c.c. of a 3 per cent. alcoholic solution of vanillin or heliotropin and 10 c.c. of hydrochloric acid, a violet coloration being obtained with sesamé oil. According to *Vandevelde*,[5] this test is inferior to Baudouin's test, since colour reactions are also given by other oils.

Zimmermann[6] has shown that refined sesamé oil sometimes fails to show the distinctive reactions, whilst the Baudouin test is rendered much less sensitive.

Detection of Adulteration.—The chief oils used for the adulteration are :—

Earth-nut oil, which can be detected by its lower specific gravity and by the determination of arachidic acid.

Cotton-seed oil, for which the best colour reactions are Halphen's, Becchi's, and the nitric acid test (see *Cotton-seed Oil*). Note should also be taken of the iodine value, specific gravity, and melting point of the fatty acids.

Poppy-seed oil, any notable addition of which will raise the iodine value.

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[1] *Pharm. J. and Trans.*, 1891, 639.

[2] *Bull. Soc. Chim.*, 1898, xix., 88.

[3] *Ann. Chim. anal.*, 1899, iv., 217.

[4] Bellier, *Ann. Chim. anal.*, 1899, iv., 217.

[5] *Bull. de l'Ass. belge Chim.*, 1900, xiv., 222.

[6] *Zeit. Unters. Nahr. Genussm.*, 1913, xxvi., 86, 450.

Rape oil will be indicated by a decrease in the saponification and iodine values, and in the melting point of the fatty acids.

Compulsory Addition of Sesamé Oil to Margarine.—An addition of sesamé oil is rendered compulsory on all margarine manufacturers by the German Government, so as to enable the product to be readily recognised by Baudouin's test. At one time the amount was fixed at 10 per cent., but it is now specified that the quantity shall be sufficient to give a distinct coloration in the test.

SMALL FENNEL-SEED OIL.[1]

Recorded Values.

Small Fennel-seed Oil.

Specific Gravity at 15·5° C.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Refraction at 40° C.		Authority.
						Scale Divisions.	Refractive Index.	
0·9248	97·41	196·4	116·2	5·40	88·83	58·5	1·4649	Crossley and Le Sueur

According to *Crossley* and *Le Sueur*, the oil expressed from the seeds of the small fennel, *Nigella sativa*, may be clear and light in colour, or dark reddish-brown, and possessing a strong odour of eucalyptus. The oil described above belonged to the second kind. On standing it yielded a deposit of solid matter.

In India this oil is used as a food and for medicinal purposes.

SOYA-BEAN OIL.

Recorded Values.

Soya-Bean Oil.

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Hehner Value.	Maumené Test.	Solidification Point.	Authority.
				°C.	°C.	
0·9242	192·5	121·3	..	59	8-15	De Negri and Fabris.
0·9272	192·9	122·2	95·5	61	..	Morawski and Stingl.
0·924	190·6	124	..	..	..	Shukoff.
0·9222 to 0·9279	..	118·2 to 135·4	..	..	..	Toch.

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[1] Crossley and Le Sueur, *J. Soc. Chem. Ind.*, 1898, xvii., 1992.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
° C.	° C.		
27-29	23-25	122	De Negri and Fabris.
28	25	115·2	Morawski and Stingl.
...	24·1	...	Shukoff.

This oil is obtained from the seeds of the soya bean (*Soja japonica*, *S. hispida*), which is indigenous to China and Japan, and is cultivated in India and Southern Asia. The seeds contain about 18 per cent. of oil.

Toch found soya beans of different origin to have the following composition:—Water, 7·43 to 8·67; proteins, 32·9 to 36·9; fat, 18·96 to 22·72; N-free extractives, 25·47 to 29·36; fibre, 4·00 to 5·15; and ash, 5·01 to 6·28 per cent.

The oil examined by *Shukoff*[1] was obtained from seed grown in an experimental station in South Russia, the yield being about 15 per cent., whilst *Toch's*[2] figures were those given by eight samples of cold-pressed Manchurian oil.

A sample of oil examined by *Keimatsu*[3] contained about 12 per cent. of saturated fatty acids, mainly stearic and palmitic, and about 80 per cent. of unsaturated fatty acids, about half of which consisted of an isomer of linolic acid, yielding a tetrabromide melting at 158° to 159° C., and about 15 per cent. of ordinary linolic acid and oleic acid. About 0·2 per cent. of a phytosterol was present.

According to *Toch* (*loc. cit.*), soya oil is bleached when heated to 500° F., and remains colourless. When blown for 5 to 7 hours with dry air it thickens and reaches a specific gravity of 0·960 and over. Thickened oil remaining pale under such condition is suitable for the manufacture of paints and of stoving varnish. A sample of cold-pressed Manchurian oil heated to 500° F. and blown vigorously for 7 hours after cooling to 300° F., gave the following results:—

	Sp. Gr. at 15·5° C.	Acid Value.	Iodine Value (Wijs).
Original oil, ...	0·929	2·6	133·6
Blown oil, ...	0·963	1·9	105·3

The blown oil dried in 3½ days, whilst the original oil required 5 to 6 days. As a paint medium soya bean oil is not quite so good as linseed oil, but *Toch* (*loc. cit.*) found that a mixture of 25 per cent. of

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[1] *Chem. Rev. Fett Ind.*, 1901, viii., 250. [2] *J. Soc. Chem. Ind.*, 1912, xxxi., 572.
[3] *Chem. Zeit.*, 1911, xxxv., 839.

tung oil and 75 per cent. of soya bean oil yielded a varnish in every respect equal to linseed varnish. Blown soya oil is used in the manufacture of linoleum, and for printing inks and enamel paints.

TOMATO-SEED OIL.

Recorded Values.

Tomato-seed Oil.

Specific Gravity.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Refractive Index.	Acetyl Value.	Iodine Value of Liquid Fatty Acids.	Authority.
0·922 at 15°C.	4·7	190·4	106·9	..	95·10	1·473	..	112	Baltaglia.
0·9184-0·9196 at 25°	..	187·0-192·0	117·5-125·0	0·1-0·3	95·0-96·6	1·4715-1·4725 at 25°C.	11·4-20·5	..	Jamieson and Bailey (9 Samples).

According to *Battaglia*,[1] the oil extracted from the seed of the tomato plant contains olein, linolin, stearin, and myristin, with 2·3 per cent. of lecithin.

The air-dried seeds of American origin examined by Jamieson and Bailey[2] yielded 18 per cent. of oil when expressed. The oil contained at least 0·4 per cent. of arachidis acid.

WHEAT OIL.

Recorded Values.

Wheat Oil.

Specific Gravity 15° C.	Free Acid as Oleic Acid.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractometer (Zeiss-Wollny).	Solidification Point.	Refractive Index.	Authority.
0·9245	Per cent. 5·65	182·8	115·2	...	74·5	0° C. 15	...	De Negri.[3]
0·9292	...	187·4-190·3	115·6	...	...	15 milky 0 semi-solid	1·47878 at 20° C. 1·47544 at 30° C.	Frankforter and Harding.
0·9374 at 0° C.	Acid Value. 40·2-41·4	...	...	...	...	...	1·47181 at 40° C.	,,
0·9068	...	166·5	101·5	2·8	92	..	1·4851 at 25° C.	Spaeth.[4]

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[1] Battaglia, *Ann. Chim. anal.*, 1901, vi., 437.

[2] *J. Soc. Chem. Ind.*, 1919, xxxviii., 781 A.

[3] *Chem. Zeit.*, 1898, xxii., 976.

[4] Extracted from wheat flour.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
° C. 39·5	° C. 29·7	123·3	De Negri.

Wheat oil is obtained from the germs of wheat, of which they compose about 12 per cent. The oil extracted with petroleum spirit is yellowish-brown, and has an odour recalling that of the grain. The characteristics of the oil vary with the kind of wheat.

It is soluble in an equal volume of glacial acetic acid at 65° C., and in thirty times its volume of hot absolute alcohol.

It readily becomes rancid, and develops free acid. Thus *De Negri* found 43·86 per cent. of free acids (as oleic acid) in a sample that had been kept for a year.

Wheat oil gives a slight brown coloration in Becchi's and Milliau's tests, but no coloration in the Baudouin reaction.

Frankforter and *Harding*[1] found the percentage of glycerol in the oil to vary from 7·2 to 7·53. They also obtained about 2 per cent. of lecithin, and 2·37 to 2·6 per cent. of paracholesterol (m.p. 134° to 135° C.; $[\alpha]_D = -26{\cdot}9$ to 28·88).

The viscosity compared with rape oil as unity gave a maximum of 2·57 at 20° C.

Wheat oil has slight drying properties. A film exposed to the air gained 0·42 per cent. in weight during the first forty-five days, and then began to lose slowly.

CLASS VI.—DRYING OILS.

CASHEW-NUT OIL.[2]

Recorded Values.

Cashew-Nut Oil.

Specific Gravity at $\frac{15·5°}{15·5°}$ C.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Butyro-refractometer.	Authority.
0·9594	...	...	294·26	1·26	Too high for scale	Crossley and Le Sueur.

The oil expressed from the kernels of the nuts of *Anacardium occidentale* is light yellow in colour and of a bland taste, whilst that

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[1] *J. Amer. Chem. Soc.*, 1899, xxi., 758.

[2] *J. Soc. Chem. Ind.*, 1898, xvii., 992.

obtained from the shell or pericarp is black and possesses an acrid taste and vesicating properties.

The oil examined by *Crossley* and *Le Sueur* was considered to be derived from the latter source.

It is known as cardole or cashew apple oil, and is used by the natives in India for illumination, soap-making, and medicinal purposes.

Notwithstanding its high iodine value, it did not dry when exposed to the air in a thin film, but, pending further investigation of the nature of the fatty acids present, is included among the drying oils.

EVERGREEN-TREE OIL.[1]

Recorded Values.

Evergreen - Tree Oil.

Specific Gravity at 15·5° C.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Refraction at 40° C.		Authority.
						Scale Divisions.	Refractive Index.	
0·9386	17·03	189·7	134·86	1·64	93·23	64·5	1·4687	Crossley & Le Sueur.

This oil is obtained from the seeds of the evergreen tree, *Amoora rohituka*, and is used in India for illuminating and medicinal purposes.

It is reddish-brown in colour, and has a neutral taste and an odour recalling that of linseed oil.

It is a drying oil, resembling niger-seed oil in its general characteristics.

The specimen examined by *Crossley* and *Le Sueur* had a viscosity of 14·79, compared with water at 70° F. as unity.

GARDEN ROCKET OIL.[2]

Recorded Values.

Garden Rocket Oil.

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Maumené Test.	Solidification Point.	Authority.
			° C.	° C.	
...	...	...	...	− 22 to − 23	Schädler.
0·9335	191·8	154·9-155·3	125-127·5	...	De Negri and Fabris.

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[1] Crossley and Le Sueur, *J Soc. Chem. Ind.*, 1898, xvii., 991.

[2] De Negri and Fabris, *Annali del Lab. Chim. delle Gabelle*, 1891-2, 151.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
° C. 20·22	° C. 14-16	157	De Negri and Fabris.

The seeds of the garden rocket, *Hesperis matronalis*, yield a green oil which changes to brown after exposure to the air and light.

The oil is used for illuminating purposes in some parts of France and Switzerland.

HEMP-SEED OIL.

Recorded Values.

Hemp-Seed Oil.

Specific Gravity.	Saponification Value.	Iodine Value.	Maumené Test.	Free Fatty Acids.	Solidification Point.	Authority.
			° C.	Per cent.	° C.	
0·9280	192·8	140·5	95-96	...	– 15 to – 28	De Negri and Fabris.
...	190-191·1	148	...	...	...	Lewkowitsch.
0·931-0·933	192-194·9	157-166	...	0·45	...	Shukoff.[1]
. .	...	157·5		...	...	Benedikt.
0·925-0·931	...	...	...	...	...	Allen.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
C. 17-21	° C. 14-16	141	De Negri and Fabris.
...	Dalican's Test. 15·6-16·6	...	Lewkowitsch.
.	16	...	Shukoff.

This oil is obtained from the seeds of *Cannabis sativa*. It is used in the manufacture of soft soap and as a drying oil for paints and varnishes.

According to *Hazura* and *Grüssner*, the liquid fatty acids consist of 70 per cent. of linolin, 15 per cent. of linolenin and isolinolenin,

[1] *Chem. Rev. Fett Ind.*, 1901, viii., 250 (Russian oil).

and 15 per cent. of olein. The oil also contains a small quantity of stearin and palmitin.

Hemp-seed oil is greenish-yellow in colour when extracted with solvents, and yellowish-brown when obtained by expression. It has a characteristic odour.

It is a good drying oil, though it dries less rapidly than linseed oil.

It is soluble in 30 parts of cold alcohol, and in 12 parts of boiling alcohol.

It is frequently used to adulterate linseed oil, and is also not infrequently present accidentally, owing to the admixture of hemp-seed with the linseed before expression.

When present in any considerable quantity it lowers the iodine value of the linseed oil, and would probably also be indicated by the lower yield of insoluble bromides from the oil and free fatty acids.

LALLEMANTIA OIL.[1]

HUILE DE LALLEMANTIA. LALLEMANTIA OEL.

Recorded Values.

Lallemantia Oil.

Specific Gravity at 20° C.,	0·9336
Solidification Point,	−35° C.
Saponification Value,	185
Iodine Value,	162·1
Hehner Value,	93·3
Reichert Value,	1·55

Fatty Acids.

Melting Point,	22·2° C.
Solidification Point,	11° C.
Iodine Value,	166

Lallemantia oil is obtained from the seeds of *Lallemantia iberica*, a plant indigenous to the Caucasus.

It is used in Russia as a lamp oil.

According to *Richter*, it is superior to linseed oil in drying properties, a specimen of the oil heated at 150° C. drying completely in twenty-four hours.

In the elaidin test it yields a dark red tough mass.

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[1] Richter, *J Soc. Chem. Ind.*, 1887, vi., 825.

LINSEED OIL.

Recorded Values.

Linseed Oil.

Origin.	Specific Gravity at 15° C.	Acid Value.	Iodine Value.	Bromine Value	Bromine Addition Value.	Bromine Substitution Value.	Saponification Value.	Hehner Value.	Refractive Index.	Authority.
American (average of 9),	0·934	...	181 (H.)[1]	...	...	...	...	...	...	Gill and Lamb.
Calcutta,	0·9326	1·1	178·6 (H.)	108·5	102·1	3·2	191·1	...	...	M'Ilhiney.
American (aver. of 12 Commercial).	0·9333	3·7	178·6 (H.)	109·1	103·7	2·7	190·4	...	...	,,
...	0·932-0·937	...	...	...	...	...	189-195	...	...	Allen.
Russian,	0·935-0·936	...	171-179	...	...	...	...	...	...	Shukoff.
...	...	...	182·25	...	...	...	...	...	...	Wijs.
...	...	...	186·97 to 202·49 (Wijs)	...	...	...	. .	...	...	Williams.
...	0·9342	...	...	...	...	...	190·2-192·7	...	...	De Negri & Fabris.
Indian,	0·9254-0·9337	4·84-28·85	...	...	...	...	187·8-191·5	94·8	1·466-4·740	Crossley & Le Sueur.

Fatty Acids.

Specific Gravity.	Melting Point. ° C.	Solidification Point. ° C	Iodine Value.	Molecular Equivalent.	Authority.
0·9233 at 15·5° C.	24	17·5	...	307·2	Allen.
0·8612 at $\frac{99° C.}{15·5° C.}$	...	...	...	...	
		Dalican's Test.			
...	...	19 0-20·6	179-182	...	Lewkowitsch.
...	20-21	16 -19	159·85	...	De Negri and Fabris.

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[1] (H.) = By Hübl's method.

Source.—The oil expressed from the seeds of the flax plant (*Linum usitatissimum*) is generally known as linseed oil. Usually it is extracted on the large scale in crushing mills by the process described in Chap. IX.; but small quantities are prepared for home consumption in different parts of the world, more especially Russia, on a much smaller scale.

The seeds as found in commerce are rarely all of one kind, more or less of the seeds of other plants being often present, the result of which occasionally is seriously to impair the quality of the oil. This sometimes arises from intentional admixture, more especially in the case of hemp seed, which is stated to be invariably added to the extent of 5 per cent. and upwards to all linseed shipped from the Black Sea ports; but quite as frequently it is accidental, and is due to other plants being grown along with flax—*e.g.*, mustard and rape. This is more especially the case with the red variety of Indian seed. The presence of mustard seed in any considerable quantity is liable to render the oilcake acrid and unsuitable as a cattle food.

Linseed is chiefly imported from the Baltic ports, Russia (Black Sea), and India; but it is also grown in considerable quantity in various parts of Europe, especially Poland, in Egypt, and in the Brazils. Seed grown in hotter climates is reputed to yield oil comparatively defective in drying power and of lighter colour than that produced in colder regions; possibly, however, this is chiefly due to admixture of other seed oils and not to actual differences in the oil contained in the flax seed.

According to *M'Ilhiney*,[1] there is a marked preference in the United States for Indian oil as being considerably lighter in colour, and it commands a higher price than the American product; but, in his opinion, this must be attributed largely to prejudice.

Owing to the fact that linseed has a very exhausting effect upon the soil, the United States source of supply is gradually being removed to the west and north-west. The American oil is slowly taking the place of that obtained from imported seed.

In practice, pure linseed oil is never met with commercially, and can only be obtained by carefully handpicking the seed before expression.

When impure linseed containing a small percentage of the usual foreign seeds is pressed, a partial separation of the oils takes place, so that the residual oilcake contains a larger proportion of the heavier crucifer oils. Hence linseed-cake prepared from impure linseed contains a much more impure oil than the original seed. Thus *Fassbender* and *Kern*[2] prepared a linseed-cake from linseed containing about 5 per cent. of crucifer seed, and showed that the residual oil gave an iodine value of only 162·5.

Linseed of various origin examined by *Sheppard*[3] gave the following yields of oil:—American, 39·67; La Plata, 36·98; Calcutta, 40·82; Bombay, 41·23; S. Russia, 39·11; and N. Russia, 36·95 per cent.

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[1] *Report on Linseed Oil to the Commission of Agriculture, New York State*, 1901.

[2] *Zeit. angew. Chem.*, 1897, 331.

[3] *J. Ind. Eng. Chem.*, 1912, iv., 14.

The average results given by 11 samples of Calcutta seed were:—Impurities, 6·90 per cent., containing 15·1 per cent. of oil, and oil from cleaned seed 41·01 per cent.

Preparation.—When subjected to pressure, some 20 to 22 per cent. of superior "cold drawn" oil can be extracted. In Poland, Russia, and other countries, this is used as an article of food, having a not unpleasant taste. Later runnings prepared by hot pressure are darker in colour and have a disagreeable acrid flavour, rendering them only suitable for technical purposes.

If the seeds are expressed comparatively "green," much more watery mucilage accompanies the oil; after keeping some months they dry somewhat and a better yield of oil with a smaller admixture of vegetable extractive matter results.

Schädler describes the average yield as being—

Cold pressed oil, ...	20 to 21 per cent.
Hot pressed oil, ...	27 to 28 ,,
Obtained by solvents, ...	32 to 33 ,,

The proportion of oil obtained, however, varies somewhat with the source of the seed. Thus Italian linseed yields somewhat more than Russian, and white Indian some 2 per cent. more than red Indian. Again, the yield varies according as the seed has been allowed to ripen fully, or as the plant has been harvested earlier for the flax crop, in which case a smaller yield of oil is usually obtained.

Linseed Cake.—Linseed cake usually contains small amounts of glucosides, which in presence of specific enzymes yield hydrocyanic acid. The amounts of hydrocyanic acid obtained by *Auld*[1] from linseed and mixed cakes varied from 0·022 to 0·056 per cent. It has been shown by *Smetham* that by keeping a mash of linseed meal at not less than 80° C. for 40 minutes no hydrocyanic acid is likely to be liberated. *Armstrong* and *Eyre*[2] have shown that unripe seeds invariably contain cyanide, but that ripe seeds are free from it.

Composition.—The elementary composition of raw linseed oil is given by *Schädler* as—

	C.	H.	O.
Cold-drawn, ...	78·11	10·96	10·93
Hot-pressed, ...	75·27	10·88	13·85

(*Cf.* Rowland Williams, *infra*).

Linseed oil contains some 10 or 15 per cent. of glycerides of solid fatty acids (palmitin, myristin, etc.). The remaining liquid glycerides consist of those of oleic, linolic, linolenic, and isolinolenic acids, in the relative proportions 5, 15 15, and 65 per cent. of the sum of the four (*Hazura* and *Grüssner*).

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[1] *J. S. E. Agric. Coll.*, Wye, 1911, xx., 289.

[2] *Proc. Roy. Soc.*, 1912, lxxxv., B, 370.

The total acid number is variously stated by different observers at 189 to 195·2, corresponding with a saponification equivalent of 287 to 297, representing a mean molecular weight of fatty acids of 274 to 285. By directly titrating the acids prepared as carefully as possible to avoid oxidation, molecular weights varying between 282 and 295 have been observed in many cases; but materially higher values up to 307 have been noticed in some instances, leading to the belief that a higher homologue of linolic acid, $C_{20}H_{36}O_2$, was present (p. 36).

Assuming linseed oil to contain only 80 per cent. of unsaturated glycerides in the relative proportions given by *Hazura* and *Grüssner* (*supra*), the calculated iodine value would be 192·05.

	Proportional Amount Present.		Iodine Value of Glyceride.		
Olein,	0·8 × ·05	×	86·20	=	3·45
Linolin,	0·8 × ·15	×	173·57	=	20·83
Linolenin,	0·8 × ·15	×	262·15	=	31·46
Isolinolenin,	0·8 × ·65	×	262·15	=	136·31
					192·05

Although this is higher than the Hübl values ordinarily obtained, yet even higher figures (up to 202·49) have been observed (*vide infra*).

Hehner and *Mitchell*[1] obtained about 20 to 21 per cent. of impure linolenic hexabromide from the mixed fatty acids of various kinds of linseed oil. The amount of pure linolenic bromide appears to be about 18 per cent. (see p. 42). They also isolated about 24 per cent. of a bromine compound which they regarded as the bromide of a mixed glyceride, oleo-dilinolenin, $C_3H_5\left\{\begin{array}{l}C_{18}H_{29}O_2Br_6\\C_{18}H_{29}O_2Br_6\\C_{18}H_{33}O_2Br_2\end{array}\right.$

It contained 56·3 per cent. of bromine and melted at 143·5° to 144° C.

They have based a test of purity on the amount of this bromide yielded by an oil (*vide infra*).

According to *Fahrion*[2] normal linseed oil has the following composition:—Unsaponifiable matter, 0·6; saturated fatty acids, 8·6; oleic, 15-20; linolic acid, 30·0; and linolenic acid, 38 per cent.

Morell[3] found the saturated fatty acids to consist of 64·4 per cent. of stearic acid, 20 per cent. of palmitic acid.

Ethyl Esters of Linseed Oil Fatty Acids.—*Henriques*[4] prepared these by treating the oil with about 15 per cent. of the amount of alcoholic potassium hydroxide required for complete saponification.

The esters were separated from the residual glycerides by distillation in a current of steam at 250° to 270° C., in which they are volatile with but little decomposition. When dried in a current of carbon dioxide, they showed the following constants:—Saponification value, 180·8; molecular weight, 309·7; iodine value, 168·4; acid value of liberated fatty acids, 198·7; and molecular weight of fatty acids, 281·8.

They were very unstable, readily undergoing oxidation on exposure to the air, and finally yielding a substance insoluble in petroleum spirit. Unlike the "linoxyn" formed by linseed oil on drying, the oxidation products of the esters are not solid substances.

Experiments by *Haller*[5] on the "alcoholysis of linseed oil (see p. 143) indicated that linseed oil contains palmitic, stearic, oleic, linolic, linolenic, isolinolenic, and arachidic acids, the last being only present in small quantity.

Boiled Linseed Oil.—The apparatus and general methods of preparing boiled oil are described in Chap. XIV., and the following

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[1] *Analyst*, 1898, xxiii., 317.

[2] *Zeit. angew. Chem.*, 1910, xxiii., 1106.

[3] *J. Soc. Chem. Ind.*, 1913, xxxii., 1091.

[4] *Zeit. angew. Chem.*, 1898, 338.

[5] *Comp. Rend.*, 1908, cxlvi., 259.

supplements what is mentioned there as to the effect of boiling on the composition of the oil.

According to *M'Ilhiney*,[1] the older method of heating linseed oil to about 500° F., while stirring in salts of lead or manganese, has been superseded to a large extent in America by a method in which a "drier" is prepared by heating the metallic oxides with a small quantity of the oil until dissolved, and adding this solution to the main body of the oil at a temperature of about 100° C. There is still, however, so much prejudice in favour of the old "kettle-boiled" oil that many manufacturers imitate its dark colour by the use of dark coloured driers. The following table gives the average composition of eight oils thus prepared :—

Specific Gravity at 15·5° C.	Saponification Value.	Acid Value.	Iodine Value (*Hübl*).	Bromine Value.	Bromine Addition Value.	Bromine Substitution Value.
0·9398	190·9	4·7	181·8	109·4	103·0	3·2

The so-called "bung-hole" oil is prepared by simply mixing raw linseed oil with driers, which often contain other constituents than metallic oxides—*e.g.*, rosin, shellac, kauri dust, and are frequently thinned by the addition of turpentine. The sale of such oil for "boiled oil" is obviously fraudulent.

Williams[2] has determined the changes in its ultimate composition which linseed oil undergoes when boiled and oxidised in various ways. These are shown in the following table :—

Elementary Composition of Raw and Boiled Linseed Oil.

	Raw		Boiled.	Solid.						
	1.	2.	3.	4.	5.	6.	7.	8	9.	10.
Carbon	75·03	75·40	74·66	74·32	69·74	69·52	68·64	65·40	64·74	64·38
Hydrogen	10·78	10·64	10·38	10·04	9·57	9·49	9·24	9·00	9·01	9·01
Oxygen	14·19	13·96	14·96	15·64	20·69	20·99	22·12	25·60	26·25	26·61

The effect of boiling on the constants of linseed oil is shown in the following comparative figures obtained by *M. Kitt*,[3] in which the numbers (0 to 6) represent the different stages from the thin raw oil to the consistency of india-rubber :—

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[1] *Report on Linseed Oil*, 1901, 2.

[2] *Analyst*, 1898, xxiii., 253.

[3] *Chem. Rev. Fett Ind.*, 1901, viii., 40.

Changes in the Values of Linseed Oil on Boiling.

No.	Acid Value.	Saponification Value.	Iodine Value.	Iodine Value of Fatty Acids.	Acetyl Acid Value.	Acetyl Saponification Value.
0	4·8	188·9, 188·6	159·3, 158·6	158·0	153·5	178·0
1	5·2	189·9, 188·3	101·4, 100·1	107·3	191·3	201·7
2	7·8	189·1	95·6	100·1	192·4	208·0
3	9·5	186·6	83·6	88·1	188·2	206·2
4	9·1	187·2	79·1	85·6	...	...
5	11·7	187·2	76·2	81·9	193·4, 192·6	213·1, 210·9
6	18·8	192·3	71·1	...	...	...

Effects of Exposure.—*Sherman* and *Falk* [1] found that on exposing linseed oil to the action of light and air the acidity and specific gravity increased, while the iodine value decreased. The increase in the specific gravity amounted to 3·43 per cent., whilst elementary analysis showed that the oil had absorbed 3·16 per cent. of oxygen. Their experiments indicated that the increase in specific gravity was probably due to a slight contraction in volume.

Sabin,[2] in experiments in which linseed oil was exposed for eight months in thin films found that the specific gravity had increased to 1·098 (corresponding with a contraction in volume of about 3·4 per cent.), whilst the gain in weight was not more than 2 per cent.

In *Thomson's* [3] experiments two varieties of linseed oil were exposed for 212 days, with the following results :—

Results.	Specific Gravity.	Gain in Weight.	Decrease in Value.
		Per cent.	Per cent.
North American oil, . . .	1·16	8·25	13·0
South American oil, . . .	1·15	7·70	12·4

Analogous experiments made by *Friend* [4] confirmed this contraction of linseed oil on oxidation. The results indicated that as the oil gained in weight its density increased, whilst the volume increased to a maximum and then showed a gradual diminution.

Analytical Distinctions between Raw and Boiled Oil.—Oils which have been boiled at a high temperature without "driers" have a greater specific gravity and viscosity and a lower iodine value than raw oils. They also dry more rapidly, and have a reddish colour with a green fluorescence. *Hehner* and *Mitchell* have found that the fatty acids of an oil which has been oxidised by boiling yield considerably less linolenic hexabromide than the unboiled oil.

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[1] *J. Amer. Chem. Soc.*, 1903, xxv., 711 ; 1905, xxvii., 605.

[2] *J. Ind. Eng. Chem.*, 1911, iii., 84.

[3] *Trans. Amer. Inst. Chem. Eng.*, 1915, viii., 251.

[4] *J. Chem. Soc.*, 1917, cxi., 162.

Method of the German Customs.—Twelve c.c. of the oil are shaken with 6 c.c. of a reagent prepared by mixing 5 c.c. of a solution of 100 grammes of lead acetate in 150 c.c. of water, with 1 c.c. of ammonium hydroxide (20 per cent.) and 32 grammes of anhydrous glycerol. The mixed oil and reagent are heated for three minutes on the water-bath, and then observed. In the case of boiled oil containing "driers" an emulsion is formed, whilst raw oil gives a clear lower layer. Metallic "driers" can be separated by shaking the oil with hot dilute nitric acid.

Oils which have been prepared without the addition of "driers," either by boiling at high temperatures or by treatment with oxygen, cannot be distinguished by the above test, and in such cases *F. Evers* [1] recommends the following test:—

Monpurgo's Test.—The linseed oil is saponified, the alcohol evaporated off, and the clear soap solution treated with sodium chloride until no more precipitate is produced. The liquid is then filtered and a large excess of acetic acid added to the filtrate. If the liquid remains clear, the oil is regarded as a raw oil, whilst a turbid solution points to the presence of an oil boiled without "driers."

Official Method of Testing Linseed Oil.—A Sub-Committee of the American Society for Testing Materials (abbreviated below to A.S.T.M.) recommended:—"All tests to be made on oil which has been filtered at a temperature between 60° and 80° F. through paper in the laboratory immediately before weighing out. The sample should be thoroughly agitated before the removal of a portion for filtration or analysis."

Foots.—One litre of the oil is left for 8 days in a glass bottle and the quantity of sediment measured. No turbidity is produced in the best grades of oil.[2]

"*Break*" *Test.*—This tests the appearance of 50 c.c. of the oil after heating to 300° C. The production of a "break" or gelatinous appearance may be due to carbohydrates or proteins from the seed or to the presence of another oil, such as tung oil or candle-nut oil, which polymerise at a lower temperature (*Hertkorn*).[3]

Ash.—*Boughton* [4] found from 0·02 to 0·21 per cent. of ash in 16 samples of genuine linseed oil. In each case a trace of manganese was present in the ash.

Tests of Purity.

Solidification Point.—According to *Chateau*, linseed oil solidifies at − 27° C.

Specific Gravity.—When freshly expressed, after refining by sulphuric acid (p. 345), linseed oil has a specific gravity at 15° of 0·932 to 0·937, averaging close to 0·935 (*Allen*). If any considerable admixture of rape or other lighter oil be present, the specific gravity falls to

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[1] *Chem. Zeit.*, 1899, xxiii., 334.

[2] Walker, *Bull. No.* 109, *U.S. Dep. Agric., Bureau of Chem.* (1910).

[3] *Chem. Zeit.*, 1910, xxxiv., 462.

[4] *J. Ind. Eng. Chem.*, 1913, v., 281.

0·930 and lower. If, on the other hand, the oil is old and has absorbed oxygen, the specific gravity is more or less considerably raised, sometimes reaching 0·950, or even more in the case of oil which has been continually heated.

Twitchell[1] has determined the corrections for temperature to be added to or subtracted from the readings of a glass hydrometer giving correct results with linseed oil at 15·5° C. According to *Bearse*[2] the specific gravity of linseed oil between 10° and 40° C. may be calculated from the result obtained at 25° C., by means of the formula—

$$D_t = D_{25} + a(t - 25) + B(t - 25)^2,$$

where a is taken as − 0·0006847 and B as + 0·000000120.

The correction for 1° F. = 0·000361, and for 1° C. = 0·000650.

The limits of the A.S.T.M. for raw linseed oil are :—At 15°/15° C., maximum, 0·936 ; minimum, 0·932. At 25°/25° C., maximum, 0·931 ; minimum, 0·927.

Melting Point of Fatty Acids.—The fatty acids separable from linseed oil have been found by various observers to melt at temperatures lying between 17° and 24° C., and to solidify at 13° to 17·5° C. As linseed oil occurs in commerce, a small proportion of these acids is usually present in the free state, free acid values being obtained varying from 0·7 to 8·0, corresponding with amounts of free acid from 0·4 to upwards of 4 per cent. of the total acids present.

As a rule, the acid value of linseed oil is less than 5, but in old oils it is frequently considerably higher. Rosin has an acid value of 145·5 to 179·2, and when present to any appreciable extent, will cause the linseed oil to have a much higher value than the normal limits given above.

Refractometer Reading.—The difference between the refractive index of linseed oil and other oils is comparatively small, but rosin and rosin oil raise the reading.

M'Ilhiney (*loc. cit.*) gives the following values taken from different sources :—

Linseed oil, ...	1·484 to 1·488 at 15° C.
Rosin oil, ...	1·535 to 1·549 at 18° C.
Rosin (Colophony), . . .	1·548
Fish oil, ...	1·480 at 15° C.

According to *Weger*,[3] the refractometer reading of fresh linseed oil in Zeiss's butyro-refractometer usually varies between 80·2° and 82·2° at 25° C., this figure being considerably increased by oxidation. Thus raw linseed oil with a reading of 80·2° gave 85·8° after being treated with 5 per cent. of manganese-lead resinate. Hence a high refracto-

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[1] *Report on Linseed Oil*, 1901, 29.

[2] *Proc. Amer. Soc. Test. Materials*, 1911, xi., 211.

[3] *Zeit. angew. Chem.*, 1899, 297, 330.

meter number need not necessarily imply the presence of mineral oil or rosin oil. The A.S.T.M. fixed the limits for genuine oil at 1·4805 and 1·4790 at 25° C.

It has been suggested by *White* and *Thomas*[1] that a test for the presence of china-wood (tung) oil might be based on the higher refractive index of the latter (1·5560 at 25° C.).

Action on Polarised Light.—Most vegetable oils, with the exception of sesamé oil, are lævo-rotatory, whereas rosin oil is dextro-rotatory. Hence, if a sample of oil rotates the beam of light to the right, the presence of rosin oil is probable.

Filsinger[2] recommends mixing the oil with chloroform and alcohol, and examining the filtered solution in the polariscope.

Unsaponifiable Matter.—This was found by *Thomson* and *Ballantyne*[3] to vary from 1·09 to 1·28 per cent. in oil from different sources.

Williams[4] gives 0·8 to 1·3 as the limits in raw oil, and 1·3 to 2·3 for oil boiled at a high temperature. In his opinion, any oil yielding more than 2·5 per cent. must be regarded as adulterated.

Oils which are "boiled" at a lower temperature give figures similar to those of the raw oil. The limit fixed for raw oil by the A.S.T.M. is 1·5 per cent.

Saponification Value.—The following figures are given by different authorities for raw oil:—*Dieterich*, 187·6; *Allen*, 187·4 to 195·2; *Amsel*, 183 to 190; *Coreil*, 201 to 221. In the case of oils boiled at a high temperature, the values are usually somewhat lower.

A low saponification value may be due to the presence of rosin oil, mineral oil, or turpentine.

Behaviour towards Different Solvents.—Linseed oil dissolves in about 5 parts of boiling and cold 40 parts of absolute alcohol, and in about 1½ times its volume of ether.

Amsel[5] considers that important conclusions may often be drawn from the determination of the solubility in alcohol. He mixes 1 gramme of the oil with 20 c.c. of alcohol, and filters the liquid after standing for twenty-four hours with frequent shaking. In the case of linseed oil he found the average amount dissolved to be 25 per cent., whilst thickened oils always yielded less than 20 per cent.

Acetic Acid Turbidity Test (*Valenta's Test*).—*Chattaway*, *Pearmain*, and *Moor*[6] obtained results varying from 46·0° to 52·0° C. with acetic acid containing 0·5 per cent. of water.

Iodine Value.—The iodine value of linseed oil has been very variously stated by different observers. The earlier results were, as a rule, considerably lower than those now commonly obtained. Thus *Hübl's* original figures were 156 to 160; *Dieterich* found different samples to give values between 161·9 and 180·9; *Benedikt* found 170 to 181; *Holde* 179 to 180; *Thomson* and *Ballantyne* 175·5 to 187·7, according

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[1] *J. Ind. Eng. Chem.*, 1912, iv., 878.

[2] *Chem. Zeit.*, 1894, xviii., 1005, 1867; *Zeit. angew. Chem.*, 195, 1895.

[3] *J. Soc. Chem. Ind.*, 1891, x., 336.

[4] *Ibid.*, 1898, xvii., 305.

[5] *Zeit. angew. Chem.*, 1895, 73.

[6] *Analyst*, 1894, xix., 150.

to the time allowed. Lower values down to 149 were recorded by other observers; but in view of the results of later researches on the difficulty of completely saturating glycerides with iodine unless a considerable time is allowed and a large excess of iodine employed, it would seem very doubtful whether these lower values were correct. The following figures have also been recorded:—*Fårnsteiner*,[1] 178·9; *Ketel* and *Antusch*,[2] 187; *M'Ilhiney*,[3] 183·8 (average of 7 samples); and *Amsel*, 180 to 183·5.[4]

Rowland Williams examined several hundred samples of raw oil, but never found any of undoubted purity to have a lower value than 180, whilst in some cases the figures exceeded 190. He invariably used a large excess of Hübl's solution, and allowed the iodine to act for 18 to 24 hours.

Wijs,[5] using his iodine chloride solution, obtained a value of 182·25, whilst *Williams*,[6] employing Wijs' method, found 9 samples of raw linseed oil to have iodine values of 186·97 to 202·49, the average being 195·91.

M'Ilhiney[7] gives 178 as the usual value for genuine oils, as found in New York State, but taking the above results into consideration 180 to 185 may be regarded as the normal figures with Hübl's solution. The A.S.T.M. has fixed 178 as the minimum value by the Hanus method.

Boiled Oil.—Linseed oil boiled by the older process gives iodine values as low as 100; but according to *M'Ilhiney*[7] boiled oil made by adding "driers" at a lower temperature gives substantially the same results as the raw oil (*vide supra*).

Williams[8] gives the following table showing the iodine Hübl values and the bromine (gravimetric) value of a number of samples of linseed oil, both raw and at different stages of boiling:—

	Raw.						Boiled.			
	1.	2.	3.	4.	5.	6.	Thin.	Thin.	Stout.	Very Stout.
Iodine value,	183·2	192·9	185·2	195·5	194·8	195·1	175·1	163·0	99·5	96·9
Bromine value,	114·2	120·7	115·1	119·2	119·6	119·4	111·3	112·4	65·6	59·9

The ratio between the iodine and bromine values is here as 1·62 : 1 (as against the theoretical 1·5875 : 1), but in the case of the boiled oil it is irregular. *M'Ilhiney* gives the iodine (Hübl) values of a number of boiled oils made by adding "driers" at a lower temperature as 174·4 to 183·3.

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[1] *Zeit. Untersuch. Nahr. Genussm.*, 1897, i., 529.

[2] *Zeit. angew. Chem.*, 1896, 529.

[3] *J. Amer. Chem. Soc.*, 1899, xxi., 1084.

[4] *Zeit. angew. Chem.*, 1895, 73.

[5] *Ber. d. d. Chem. Ges.*, 1898, xxxi., 750.

[6] *J. Soc. Chem. Ind.*, 1900, xix., 300.

[7] *Report on Linseed Oil*, 1901, 12.

[8] *Analyst*, 1895, xx., 277.

The iodine value of boiled linseed oil is conveniently determined in acetic acid as solvent, and this has been recommended by *Wilhelm* and *Meister* [1] as the best solvent for products such as linoxyn.

Bromine Values.—*Williams* [2] states that he has frequently used Hehner's gravimetric process with satisfactory results, and some typical instances are shown in the table above. He has also (*ibid.*) made comparative determinations on 9 samples of raw oil of the iodine value of Wijs' method and of the bromine addition and substitution values by M'Ilhiney's method, the average results being as follows:—

Iodine Value (*Wijs*).	Bromine Value Calculated from Iodine Value.	Bromine Value Determined.	Bromine Addition Value.	Bromine Substitution Value.
195·91	123·8	118·7	113·21	2·74

M'Ilhiney [3] gives the following as the ordinary figures for linseed oil:—

Iodine Value (*Hübl*).	Bromine Value.	Bromine Addition Value.	Bromine Substitution Value.
170-185	105-115	100-110	Less than 7

Bromine Thermal Value.—It has been shown by *Jenkins* [4] and by *Archbutt* [5] that the iodine values calculated from the rise of temperature with bromine (*Hehner* and *Mitchell*) agree well with the Hübl iodine values. The value of this rapid test is also confirmed by *Williams*.[6]

Amount of Insoluble Bromide.—*Hehner* and *Mitchell* [7] base a test of the purity of linseed oil on the amount of insoluble bromide (? bromide of oleo-dilinolenin, m.p. 143·5° to 144° C.), which it yields.

From 1 to 2 grammes of the glycerides are dissolved in 40 c.c. of ether, to which a few c.c. of glacial acetic acid are added, the precipitate forming being more granular from such a mixture than when ether alone is employed. The solution is cooled in an ice-chest and bromine added, the flask being preferably left all night in the ice. This, however, is not essential for ordinary working. The liquid is filtered off by the suction funnel attached to a pump, the flask washed out with four successive portions of 10 c.c. of ether at 0° C., and the residue dried in the flask to constant weight. But even when ether at ordinary temperature is used no considerable error is introduced.

The precipitate can also be collected either in a Soxhlet tube, if the

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[1] *Chem. Rev. Fett Ind.*, 1910, xvii., 260.

[2] *J. Soc. Chem. Ind.*, 1900, xix., 300.

[3] *Report on Linseed Oil*, 1901, 31.

[4] *J. Soc. Chem. Ind.*, 1897, xvi., 194.

[5] *Ibid.*, 311.

[6] *Ibid.*, 1900, xix., 300.

[7] *Analyst*, 1898, xxiii., 315.

quantity taken is small, or on a counterpoised filter, but *Hehner* and *Mitchell* recommend the method devised by them for the determination of stearic acid (*q.v.*). Instead of cotton, however, they find thin flexible chamois leather to be the best filtering material. This is tied over the end of the small thistle funnel, from which any adhering precipitate can afterwards readily be removed by washing.

Various samples of pure linseed oil were examined by this method, with the following results :—

Insoluble Bromide from Linseed Oil.

Sample.	Oil taken.	Weight of Precipitate.	Percentage of Deposit.
A	1·3226	0·3156	23·86
A	3·1005	0·7573	24·42
B	0·6792	0·1765	25·8
C	1·0000	0·2480	24·8
C	1·0000	0·2500	25·0

A sample of walnut oil gave, in two determinations, 1·9 and 1·42 per cent. of insoluble bromide. Poppy oil (four specimens) gave no deposit, nor did brazil-nut oil, maize oil, cotton-seed oil, olive oil, Japan wood oil, or almond oil. Mixtures of linseed oil and other oils gave percentages in proportion to the percentage of linseed oil, as will be seen from the following table :—

Insoluble Bromide from Mixtures.

Oils Used.	Linseed Oil, Per cent.	Insoluble Bromide, Per cent.	Linseed Oil Calculated from Bromide.
Linseed A and walnut,	69	16·6	69
,, ,,	38·2	9·3	38·1
Linseed A and maize oil,	52	12·4	50·8
,, ,,	50·5	12·2	50 0
,, ,,	51·7	12·6	51·6

It will be seen from the above figures that the determination of the amount of the precipitate can usefully serve for testing the purity of unoxidised linseed oil.

M'Ilhiney[1] made experiments with this method; his results substantially confirmed those of *Hehner* and *Mitchell*. Two samples of the raw linseed, six samples of boiled linseed, two of maize, and one of cotton-seed oil gave results in agreement with theirs. No precipitate was obtained with mineral oil, rosin oil, or turpentine.

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[1] *Report on Linseed Oil*, 1901, 19.

The writer (*M.*) has met with one specimen of linseed oil which yielded over 30 per cent. of insoluble bromide; but, with this exception, the whole of the unoxidised oils, of which he has examined a large number, have yielded from 23·5 to 26 per cent. of the compound. This would correspond with about 10·5 per cent. of the mixed glyceride for the oil.

Rape oil gives about 1 per cent. of insoluble bromide, and the similar mustard-husk oil about 1·5 per cent.

Some of the marine animal oils approach linseed oil in many of their properties, especially in their iodine absorption. It is interesting to note that the (impure) linolenic acid which *Hehner* and *Mitchell* prepared from linseed oil had a marked odour of fish oil, and that pure linseed oil, when heated in steam, often emits a similar fishy smell.

These oils also yielded insoluble bromides, which, however, differed from the linseed oil derivative in becoming dark on heating and decomposing before melting. The following amounts were obtained:—Whale oil, 25·0; cod oil, 35·5; cod-liver oil, 42·9; and shark oil, 22·0 per cent.

For another method by *Hehner* and *Mitchell*, based on the determination of linolenic acid in the mixed fatty acids, see p. 158.

Sutcliffe[1] finds that results agreeing within about 1 per cent. are given by the following modification of the test:—A solution of 1 gramme of the oil in 40 c.c. of ether is treated with 5 c.c. of glacial acetic acid, and the flask cooled in water at about 11° C. After the addition drop by drop of an excess of bromine the flask is closed and left for 12 hours in water, after which its contents are filtered through a disc of paper in a Gooch crucible, and the precipitate washed three times by decantation, and twice in the crucible with 10 c.c. of ether at 5° C. Finally, it is dried for 3 hours in the water-oven and weighed.

Under these conditions it was found that, in the case of linseed oils of different origin, the relationship between the yield of insoluble bromide and the iodine value could be expressed by the formula:—Per cent. of bromide = (0·63 iodine value) − 78·0.

The precipitated bromides must be quite white and must crumble readily.

Gemmell[2] has shown that the difficulty in obtaining concordant results by the various methods is due to the solubility of the bromides in various solvents, and prefers to precipitate the hexabromides from the fatty acids previously chilled in ice-water. In this way he obtained the following results:—Raw linseed oils (7 kinds), 32·60 to 37·65; boiled linseed oils (6 samples), 25·95 to 33·90; soya-bean oil, 4·10; rape oil, 2·35; and walnut oil, 3·0 per cent. In the case of marine animal oils his results were:—Cod-liver oil, 35·20; whale oil, 21·70; brown whale oil, 25·80; menhaden oil, 51·70; shark-liver oil, 17·70; and sperm oil, 1·70 per cent.

In *Gemmell's* modification there is some risk of losing linolenic acid

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[1] *Analyst*, 1914, xxxix., 28, 388.

[2] *Ibid.*, 388.

by oxidation prior to the bromination, and the method lacks the simplicity of the direct estimation of bromides in the oils themselves. Moreover, by chilling the mixed fatty acids there is a probability of precipitating linolic tetrabromide, which is not easy to remove completely from the hexabromide.

Stiepel[1] has shown that linseed oil yields a much smaller amount of bromide after heating, whilst marine animal oils which have been heated give no deposit at all. Hence a negative result in the test cannot be considered as a conclusive proof of the absence of marine animal oil.

Sprinkmeyer and *Diedrichs*[2] obtained the following amounts of insoluble bromides by *Hehner* and *Mitchell's* method:—Linseed oil, 28·9; candle-nut oil, 8·8; hemp-seed oil, 8·82; walnut oil, 2·22; soya-bean oil, 3·62; sesamé oil, 0·14; mustard oil, 1·30; and rape oil, 1·92 per cent.

Eibner and *Muggenthaler*[3] found the fatty acids from various raw linseed oils of undoubted purity to yield the following amounts of bromides:—Dutch, 51·73; River Plate, 51·66; East Indian, 50·50. Other oils gave the following results:—Poppy oil, 0·0; perilla oil, 64·12; rape oil, 6·34; and soya-bean oil, 7·17 per cent. The higher figures obtained by these chemists appear to be due to the fact that the bromination and manipulation were carried out at a temperature of − 10° C.

The Maumené Test.—Linseed oil resembles the marine animal oils in giving high Maumené figures by the older methods of applying the test, and formerly this was often used as a means of detecting any considerable admixture of oils such as rape-seed oil.

This must be attributed, however, mainly to the lower degree of saturation of linseed oil, the high temperature produced by the addition of the sulphuric acid to the unsaturated bonds leading to further obscure reactions.

Mitchell has shown that when the fatty acids are diluted with carbon tetrachloride the heat liberated on the addition of sulphuric acid is proportional to the bromine thermal value.

For various Maumené figures obtained with linseed oil by different observers, see *Maumené Test*, p. 211.

Absorption of Oxygen.—Livache's test and its modifications afford an indication as to whether semi-drying oils or drying oils of inferior quality are present, inasmuch as the increment of weight after a few days, when no further increase is noticeable, is from 14 to 15 per cent. in the case of fresh genuine linseed oil, but considerably less in the presence of any large proportion of other oils.

A simpler test based on the shorter time required by genuine linseed oil to dry thoroughly, as compared with adulterated samples and other drying oils, is the "film test" described on p. 188. The character of the dried film is also taken into account, whether resinoid and brittle when cold, or hard and varnish-like but tough, or inclined to be readily

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[1] *Chem. Zeit*, 1912, ii., 175.
[2] *Zeit. Unters. Nahr. Genussm.*, 1912, xxiii., 679.
[3] *Chem. Zentralbl.*, 1913, i., 567.

broken up and crumbly. Such a practical test, although not quantitative in character, is often of great value.[1]

Moreover, an old sample of oil that has already taken up some amount of oxygen, although by no means deteriorated for many ordinary applications thereby, would be indicated as of inferior quality if Livache's test alone were relied on; but would not be shown to be deficient in drying power by the "film test." Such an oil, however, would possess a lower iodine number than fresh oil, even if otherwise genuine, inasmuch as the oxygen taken up appears to be largely added on to the unsaturated carbon groups just as iodine is.

When tested by Bishop's method (*q.v.*), linseed oil shows an oxygen absorption of about 16·5 per cent. at 28° C., and of about 17 per cent. at 17° C. (See also *Drying of Oils*, p. 193.)

Detection of Various Adulterants—*Hydrocarbons.*—Hydrocarbons are not infrequently added as adulterants. Of these, mineral oils lower the specific gravity, and rosin oils raise it, so that a suitable mixture of the two has little or no effect. The test described on p. 171 enables this admixture to be readily detected and the quantity determined. If any considerable amount is present the film test indicates the fact, as the film remains a long time sticky with only small quantities, and never properly hardens and dries with larger proportions.

Volatile hydrocarbons, such as turpentine, are separated from the oil by distillation with steam. In the presence of turpentine the oil will show high bromine figures by M'Ilhiney's method, whilst rosin oil and rosin will be indicated by a low bromine absorption and addition value and a high bromine substitution value.

Rosin (colophony) may be detected and determined by dissolving the oil in a little pure alcohol, and titrating the resin acids with standard alkali. Water is then added to the neutral mass, and the glycerides separated by gravitation or petroleum spirit. The aqueous liquid is acidified, the mixed fatty acids and resinous acids separated and weighed, and the resin in the mixture determined as in the case of rosin soaps (*Yellow Soaps*, Chap. XXII.).

The determination of the insoluble bromides by Hehner and Mitchell's method will also furnish valuable information.

Fish oils (cod, menhaden, etc.) give high thermal values in Maumené's test, and high iodine values, so that their presence is not indicated by either reaction. Boiling with sodium hydroxide develops a peculiar reddish colour when these oils are present. Chlorine gas blown through the oil causes a great darkening in tint not observed with pure linseed oil. The sulphuric acid test (p. 209) gives simply a dark brown clot with genuine linseed oil, but a reddish-brown spot if fish oils are present.

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[1] The film test is often modified by mixing the oil to be tested with three times its weight of white lead, so as to form a paint which is then applied by a brush to a clean surface; a precisely similar trial is made side by side with a standard sample of oil, and the rates of drying compared. If non-drying oils be present, even in only small quantity, the rate of drying is markedly slackened.

Oil.	Specific Gravity at 15·5 C.	Saponification Value.	Acid Value.	Hübl Value.	Bromine Absorbed.	Bromine Addition Value.	Bromine Substitution Value	Remarks.
					Per cent.			
Linseed, raw, .	0·931-0·937	187-196	less than 7	170-185	105-115	110-110	less than 7	
,, boiled, .	0·932-0·950	186-196	,,	170-185	105-115	110-110	,, 7	
Mineral oil, .	0·800-0·950	0	0	less than 25	less than 20	less than 10	,, 10	Unsaponifiable; may contain acids.
Rosin oil, . .	0·970-1 000	less than 20	less than 20	40-60	90-200	,, 20	40-100	Largely unsaponifiable.
Menhaden oil, .	about 0·931	about 189	,, 10	160-180	105-115	90-100	5-10	High Maumené and low absorption figures.
Maize oil, . .	,, 0·934	,,	,, 10	115-125	about 75	about 72	about 2	
Cotton-seed oil, .	0·922-0·930	191-197	,, 10	106-111	,, 65	,, 62	,, 2	
Turpentine, . .	about 0·873	0	0	...	,, 265	,, 165	,, 50	Volatile with steam.
Benzine, . .	0·730-0·745	0	0	...	less than 55	less than 20	less than 20	Volatile with steam.
Rosin, . . .	1·04 - 1·11	175-195	155-165	140-160	135-165	,, 15	65-80	Separated by Twitchell's method.

The behaviour of the insoluble bromides when heated in a tube should be noted, since those from marine animal oils darken before melting.

Hemp-seed oil is a frequent constituent of linseed oil, owing to the admixture of hemp-seed with linseed before reaching the crushing mills.

Its presence is indicated by a lower iodine value, and lower yield of insoluble bromide.

The preceding table given by *M'Ilhiney* shows the ordinary constants of linseed oil and some of its adulterants.

MEXICAN POPPY OIL.[1]

Recorded Values.

Mexican Poppy Oil.

Specific Gravity at 15·5° C./15·5° C.	Acid Value.	Saponification Value.	Iodine Value	Reichert-Meissl Value.	Hehner Value.	Viscosity compared with Water at 70° F.	Refraction at 40° C.		Authority.
							Scale divisions.	Refractive Index.	
0·9247	6·0	190·3	122·5	0·0	95·07	10·59	62·5	1·4675	Crossley & Le Sueur.
0·9259	83·6	187·8	119·9	0·0	...	10·71	...	...	,,

This oil is obtained from the seeds of the Mexican or prickly poppy, *Argemone mexicana*, which grows abundantly in India.

The second of the two samples in the above table had evidently undergone considerable changes, since it had a high acid value, and was completely soluble in 8 to 10 times its volume of cold absolute alcohol.

Mexican poppy oil is used in India for medicinal purposes and as a lamp oil. It belongs to the class of drying oils.

NIGER-SEED OIL.

Recorded Values.

Niger-Seed Oil.

Specific Gravity.	Acid Value as Oleic Acid.	Saponification Value.	Iodine Value.	Hehner Value.	Maumené Test.	Refractive Index.	Solidification Point.	Authority.
0·9270 at 15·5° C. 0·8738 at 99° C.	Per cent. ...	..	...	...	81	...	° C. below −9	Allen.
..	...	...	132·9	...	...	...	...	Archbutt.
...	...	189-191	...	...	...	...	...	Stoddart.
0·9271 at 15·5° C.	0·96	181·5 181·9	126·4	...	...	...	−8	Mitchell.[2]
...	...	...	...	...	82	...	...	Baynes.
0·9248 to 0·9263	1·31 to 2·94	188·9 to 192·2	126·6 to 133·8	95·44	...	1·4678 1·4689	...	Crossley & Le Sueur.[3]

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[1] Crossley and Le Sueur, *J. Soc. Chem. Ind.*, 1898, xvii., 992.

[2] *Unpublished.* Oil extracted with ether.

[3] *J. Soc. Chem. Ind.*, 1898, xvii., 992 (Indian oils (4), *Guizotia abyssinica*).

Fatty Acids.

Specific Gravity.	Melting Point.	Solidification Point.	Bromine Thermal Value (Factor = 5·52).	Authority.
	° C.	° C.	° C.	
0·8886 at 100° C. (Water at 100° = 1)	...	...	...	Archbutt.
0·8480 at 100° C. (Water at 15·5° = 1)	25·4	22·6	22·1	Mitchell.

Niger-seed oil is obtained from the seeds of *Guizotia oleifera*, which is grown chiefly in Abyssinia and India.

It is pale yellow in colour, and is said to have a nutty taste, though the oil extracted with ether has no characteristic flavour. It dries well, though much less rapidly than linseed oil.

The writer (*M.*) has found that, when treated in an ether solution with bromine, it gives only a slight turbidity. Hence its presence in linseed oil could be detected by Hehner and Mitchell's method of determining the amount of insoluble bromides yielded by the oil and by the fatty acids.

It is sometimes used to adulterate rape oil; its presence would be indicated by the increase in the saponification and iodine values, and by the diminished viscosity.

OITICICA OIL.[1]

Recorded Values.

Melting Point.	Fatty Acids.	Saponification Value.	Iodine Value.	Specific Gravity at 15·5° C.	Melting Point of Fatty Acids.	Authority.
	Per cent.					
Begins 21·5° C. Complete 65·09.	5·7	188·6	179·5	0·9694	53·7 begins 67·0 complete	Bolton & Revis.

This oil is derived from the seeds of *Conepia grandifolia*, which grows in Brazil. The seeds contain about 62 per cent. of an oil which is normally semi-solid, but tends to separate into a solid and liquid portion. It closely resembles tung oil in odour and in its property of gelatinising when heated. At 300° C. it polymerises, forming a stiff transparent jelly.

In the oxidation test it gained 4 per cent. in weight after three hours at 100° C., and on drying formed a wrinkled film.

In the solid condition the oil is not readily oxidised. It is an oil which should be of value in the manufacture of paints, varnishes, and linoleum.

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[1] Revis and Bolton, *Analyst*, 1918, xliii., 251.

PERILLA OIL.

Recorded Values.

Perilla Oil.

Specific Gravity.	Saponification Value.	Iodine Value.	Hehner Value.	Refractive Index.	Melting Point of Fatty Acids.	Authority.
0·9306 at 20° C.	189·6	206·1	..	..	– 5° C.	Wijs.
0·9280 at 15°	188·6	181·2	95·87	1·48249	..	Niegemann.
0·9305	190·6	196·3	..	1·4753 at 40° C.	..	Rosenthal.
0·9342-0·9346 at 15·5° C.[1]	192·17-193·88	195·72-202·45	..	1·4835-1·4841 at 15°	..	Lewkowitsch.
0·9318-0·9372[2]	189·67-193·48	185·65-200·46	..	1·4826-1·4840	..	”

Perilla oil is derived from the seeds of *Perilla ocimoides,* a plant occurring in China, Japan, and parts of India. Until a few years ago but little was known of this oil outside the countries of production.

The seeds were found by *Fox*[3] to yield 45 per cent. of a pale yellow oil, which is characterised by its remarkably high iodine value. The fatty acids yield a large amount of linolenic hexabromide (45 to 51 per cent.), and the oil also contains the glycerides of oleic, linolic, palmitic, and stearic acids.

In Manchuria perilla oil is used as an edible oil. As indicated by its composition, it is a good drying oil, but tends to form a streaky film. It is extensively used in Japan for the manufacture of paints, printing inks, and varnishes, and in the preparation of artificial leather.

PINE-NUT OIL.

Recorded Values.

Pine-Nut Oil.

Specific Gravity.	Saponification Value.	Iodine Value.	Maumené Test.	Heat of Combustion Calories per Gramme.	Refractive Index at 20° C.	Solidification Point.	Authority.
			° C.			° C.	
0 9215 at 15° C.	191	119-120	...	...	...	– 18 to – 20	De Negri & Fabris.[4]
0·9174 at 24° C.	...	105·8	...	9448	1·4659	...	Merrill.[5]
0·9250	...	...	...	..	...	– 27	Schädler.[6]
0·9333	192·81	101·3	71·0	...	1·4769	...	Blasdale.[7]

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[1] Cold-drawn oils.

[2] Commercial samples.

[3] *J. Ind. Eng. Chem.*, 1912, iv., 229.

[4] *Zeit. anal. Chem.*, 1894, xxiii., 564 (*Pinus picea*).

[5] *Maine Agric. Exper. Stat. Bull.*, 1900, [65], 111 (*Pinus edulis*).

[6] *Technologie der Fette* (*Pinus picea*).

[7] *J. Amer. Chem. Soc*, 1895, xvii., 935 (*Pinus monophylla*), California.

Fatty Acids.

Origin.	Melting Point.	Solidification Point.	Iodine Value.	Authority.
	° C	° C.		
Pinus picea, . .	16-19	10-16	121·5	De Negri and Fabris.
Pinus monophylla, .	19	...	..	Blasdale.

This oil is obtained from the nuts of different varieties of pine trees (*Pinus sylvestris, P. picea, P. abies, P. edulis*, etc.).

The oil expressed from the nut of *Pinus sylvestris* has a strong odour of turpentine. It dries rapidly and is well suited for the manufacture of varnish.

The oil from *Pinus picea* does not dry so rapidly. The Californian *Pinus monophylla* yields a brown drying oil of unpleasant odour and taste (*Blasdale*).

When treated with dilute nitric acid (3 : 1; Hauchecorne's reagent), pine-nut oil assumes a rose colour, but is still fluid after twenty-four hours.

It gives no coloration in Becchi's or Milliau's reactions.

POPPY-SEED OIL.

Recorded Values.

Poppy-Seed Oil.

Specific Gravity.	Acid Value.	Saponification Value.	Iodine Value	Hehner Value	Refractometer Reading.	Solidification Point.	Authority.
0·924-0·937	...	193-195	131-141	...	...	° C. −15 to −20	De Negri and Fabris.
0·926 at 15·5°C.	Acidity as Oleic Acid. 2·66	...	129·6	...	...	...	Sherman and Snell.[1]
...	...	...	127·98 to 128·55	...	...	...	Vulté and Logan.
...	...	...	140·9	...	...	...	Mitchell.
0·924-0·926 at 15° C.	...	192·8 to 194·6	134 to 136	95·38	...	...	Andés.
...	...	...	133	...	72·0 at 25° C.	...	Beckurts and Heiler.[2]
0·925-0·926 at 15° C.	...	193-194	131	...	...	...	Shukoff.[3]

[1] *J. Amer. Chem. Soc.*, 1901, xxiii., 164.
[2] *Zeit. anal. Chem.*, 1901, xl., 426.
[3] *Chem. Rev. Fett Ind.*, 1901, viii., 250.

Fatty Acids.

Specific Gravity.	Melting Point.	Solidification Point.	Iodine Value.	Authority.
	° C.	° C.		
0 8886 at 100° C. (Water at 100° C. = 1)	...	...	...	Archbutt
...	...	...	139	De Negri and Fabris.
...	20·5	16·5	...	Hübl.
...	20·5	16·5	...	Andés.
...	...	Dalican's Test. 17-19	...	Shukoff.

Source.—Poppy oil is obtained from the seeds of the poppy plant (*Papaver somniferum*), which is grown extensively in Persia, Asia Minor, and Egypt. It has many points of resemblance with olive oil, for which it is often used as a substitute as a salad oil. It is also employed for illuminating purposes, and in the manufacture of varnish after being boiled.

De Negri and *Fabris* state that it is a common adulterant of olive oil in France.

Composition.—According to *Cloez*, poppy oil closely resembles linseed oil (*q.v.*) in its elementary composition, both in the fresh and oxidised condition.

	Carbon.	Hydrogen.	Oxygen.
Poppy seed oil, fresh, ...	77·50	11·40	11·10
,, after 18 months' exposure, .	66·68	9·94	23·38

Hazura and *Grüssner* found the liquid fatty acids to consist of oleic acid, 20; linolic acid, 65; and linolenic and isolinolenic acids, 5 per cent.

The mixed fatty acids yield a deposit of linolic tetrabromide (m.p. 113° C.) when treated with bromine, but do not give any hexabromide. Nor does the oil itself yield any insoluble bromide like that obtained from raw linseed oil (*Hehner* and *Mitchell*).[1]

Stearic and palmitic acids have been identified in the solid fatty acids.

Properties.—*Oxygen Absorption.*—By Bishop's method[2] of determining the amount of oxygen absorbed, the maximum increase in weight was found to be 14·50 per cent. after thirty hours at 22° to 28° C., and 14·30 after forty-eight hours at 17° to 23° C.

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[1] *Analyst*, 1898, xxiii., 314, 315.

[2] *Analyst*, 1896, xxi., 106. See also *Oxygen Absorption*, chap. vii.

Iodine Value.—By Hübl's method, *Wijs* obtained 119·36 after four hours, and 119·67 by his own method after an absorption of seven minutes.

Bromine Thermal Value.—This is slightly lower than the calculated iodine value requires.

Maumené Test.—The following figures have been recorded:—*Maumené*, 74; *Archbutt*, 86 to 88; *De Negri* and *Fabris*, 87 to 88·5. *Mitchell*[1] has shown that the bromine thermal value and the rise with sulphuric acid of the fatty acids are both in proportion to the iodine value. The *halogen standard figure* (*q.v.*) with an old specimen of oil was 25·5.

Detection of Adulteration.—Baudouin's test will detect sesamé oil, which is the most common adulterant. Any admixture of poppy-seed oil with olive oil will be indicated by the increased specific gravity and iodine value. For the detection of linseed oil in poppy-seed oil, Hehner and Mitchell's insoluble bromide test, or modifications of that test, may be serviceable (see *Linseed Oil*).

SAFFLOWER OIL.

SAFFRON OIL. CARTHAMUS OIL.

Recorded Values.

Safflower Oil.

	Specific Gravity at 15·5° C.	Acid Value.	Saponification Value.	Iodine Value.	Riechert-Meissl Value.	Butyro-refractometer at 40° C.	Acetyl Value.	Authority.
Average of 12, .	0·9267	6·14	189·8	141·3	0·0	..	16·1	Crossley & Le Sueur.[2]
" Distilled " oil,	0·9634	..	188·0	128·9	..	..	..	,,
Carthamus oxyacantha, .	0·9270	3·66	189·4	135·5	..	..	..	,,
Indian, expressed,	0·914	0·6	202	122	0·2	64	..	Mann and Kanitkar.
,, extracted,	0·914	0·6	203	116	0·2	64	..	,,
Russian oil, .	At 15° C. 0·927	..	195·4	141·6	..	..	..	Shukoff.

This oil is obtained by expression or extraction from *Carthamus tinctorius*, which, until a few years ago, was extensively cultivated in

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[1] *Ibid.*, 1901, xxvi., 169.

[2] *J. Soc. Chem. Ind.*, 1898, xvii., 992.

India for its dyestuff, but is now grown for its oil seeds. It is separated either by cold expression or by hot extraction—a so-called downwards distillation process.

Seeds of the Indian plant examined by *Mann* and *Kanitkar*[1] yielded on the average 31·6 per cent. of oil, whilst the kernels contained 51·31 per cent.

According to *Shukoff*,[2] the cultivation of saffron is developing in South Russia. The seeds yielded up to 20 per cent. of oil.

Le Sueur[3] found 95·30 per cent. of insoluble fatty acids in a specimen of the oil, consisting of approximately 10 per cent. of solid acids and 90 per cent. of liquid acids. The solid fatty acids, fractionated by Heintz's method, were found to consist of palmitic and stearic acids, whilst the unsaturated acids contained oleic and linolic acids. Linolenic and isolinolenic acids were proved to be absent, both by the results of the oxidation test by Hazura's method and by the nature of the compounds obtained on bromination.

Expressed oil examined by *Mann* and *Kanitkar* contained 72·05 per cent. of unsaturated and 11·83 per cent. of saturated acids, mainly palmitic acid.

Safflower oil obtained by expression is pale yellow to orange in colour, and possesses a slight odour and taste.

As compared with water at 70° F., its viscosity varies from 9·57 to 10·81.

Le Sueur states that it possesses good drying properties. It is dextro-rotatory, and resembles walnut and poppy oils in its general characteristics.

In India it is used as a drying oil and also for cooking. Mixed with litharge it absorbed 8·2 per cent. of oxygen (*Mann* and *Kanitkar*). White lead paints prepared with safflower oil dry with a more glossy surface than those made with boiled linseed oil.

When prepared by the "distillation" process, the oil undergoes some amount of decomposition or polymerisation, yielding a black liquid of high specific gravity and pitchy odour. This product is used by the natives as a preservative for leathern water-vessels, ropes, etc., but, unlike the expressed oil, is of no use for burning.

An oil which had been heated for 12 hours at 300° C. until converted into this semi-solid mass, termed *roghan*, had the following characters:—Specific gravity at 26° C., 0·952; Reichert-Meissl value, 3·8; saponification value, 138; acid value, 46·5; and iodine value, 48·6 (*Mann* and *Kanitkar*).

The oil extracted by *Shukoff* contained 0·13 per cent. of free fatty acids, calculated as oleic acid.

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[1] *J. Soc. Chem. Ind.*, 1919, xxxviii., 37 T.
[2] *Chem. Rev. Fett Ind.*, 1901, viii., 250.
[3] *J. Soc. Chem. Ind.*, 1900, xix., 104.

STILLINGIA OIL.[2]

Recorded Values.

Oil.

	Tortelli and Ruggeri.[1]	Sprinkmeyer and Diedrichs.[2]
Specific gravity at 15° C.,	0·9432	..
,, ,, 100° C.,	0·8737	..
Acid value (oleic acid),	6·15	1·24
Saponification value,	210·4	209·44
Hehner value,	94·4	95·27
Reichert value (5 grammes),	0·93	0·99
Iodine value,	..	154·9
Oxygen absorbed (*Livache*), per cent.,	12·20	..
Unsaponifiable matter, per cent.,	1·45	..
Refractometer reading (*Zeiss-Wollny*),	75° at 35°	77·4 at 40° C.
Maumené test,	136·5° C.	..
,, specific temperature reaction,	267	..
Rotatory power (200 mm.) at 16° C.,	−18·6°	..

Fatty Acids.

Melting point,	14·5° C.	..
Solidification point,	12·2° C.	..
Iodine value,	161·9	..
,, of liquid acids,	178·1	..
Saponification value,	214·2	..
Molecular equivalent,	274·1	273·2
Acetyl value,	28·7	..

Stillingia oil is obtained from the seeds of *Stillingia sebifera*, the kernels of which contain about 60 per cent., whilst about 22 per cent. of solid fat (*Stillingia tallow*, *q.v.*) is contained in the capsules.

It resembles linseed oil in character, being a very good drying oil, but can be distinguished from that oil by its strong lævorotatory power.

It is soluble in alcohol to the extent of 48·9 parts per 1,000.

When treated with bromine it yields about 20 per cent. of insoluble bromides melting at 147° C.[2]

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[1] Tortelli and Ruggeri, *J. Soc. Chem. Ind.*, 1901, xx., 261.

[2] Sprinkmeyer and Diedrichs, *Zeit. Unters. Nahr. Genussm.*, 1914, xxvii., 132.

SUNFLOWER OIL.

Recorded Values.

Sunflower Oil.

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Critical Temp. of Solution.	Maumené Test.	Oleo-refractometer.	Solidification Point.	Authority.
			° C.	° C.	° C.		
0·9258	193-193·3	129	..	67·5	..	..	Spüller.
0·919	..	122·5-133	..	..	+22	..	Dieterich.
0·925	192	..	104	..	..	..	Jean.
0·924-0·926	188-189	..	..	72-75	..	..	De Negri & Fabris.
0·924-0·926	191·7-193	136	..	..	..	..	Shukoff.
..	193	..	..	..	..	−17 partially solid	Holde.
..	..	..	..	..	..	..	Pearmain.
..	..	106	..	..	..	..	Bolton and Revis.[1]

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Saponification Value.	Authority.
° C.	° C.			
..	..	133·2-134	201·5	Spüller.
23	18	..	..	Dieterich.
22-24	18	124	..	De Negri and Fabris.
22	..	..	..	Jean.
..	Dalican's Test. 19·4-19·8	..	..	Shukoff.

Sunflower oil is obtained from the seeds of *Helianthus annuus*, which is extensively cultivated in Russia (see Chap. XIV., p. 394).

According to *Jean*,[2] 100 kilos. of seed yield about 15 to 20 kilos. of edible oil in cold expression. This oil is pale yellow in colour and neutral in taste, whilst the hot-pressed oil (used as a lamp oil and in the manufacture of varnish) is much darker.

Composition.—Sunflower oil contains olein, linolin, palmitin, and probably a small quantity of linolenin. *Jean* found 0·72 per cent. of unsaponifiable matter and 3·1 per cent. of free fatty acids in a specimen of the oil; whilst *Holde*[3] found 5·6 per cent. of free acids in oil extracted with petroleum spirit.

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[1] From white seeds.

[2] *Ann. Chim. anal.*, 1901, vi., 166.

[3] *J. Soc. Chem. Ind.*, 1894, xiii., 892.

Drying Properties.—Sunflower oil dries more slowly than linseed or poppy oils. A specimen tested by *Jean* by Livache's method absorbed 4·4 per cent. of oxygen in five days; and when exposed to the air by itself in a thin film dried in nine days.

Detection of Adulteration.—Sunflower oil is sometimes used to adulterate olive oil (*Allen*), and as it is used in margarine (*Jolles*) may occur in butter.

According to *Jean*, it slightly reduces Becchi's reagent, but does not give any coloration with Halphen's or Baudouin's reagent.

Lewkowitsch recommends the nitric acid test for distinguishing sunflower oil when mixed with other oils from cotton-seed oil (see *Cotton-seed Oil*, p. 525).

In olive oil an increase in the iodine value would result from the addition of any considerable quantity of sunflower oil.

It is soluble in cold alcohol to the extent of 0·6 per cent. (*Jean*).

TUNG OIL (for Recorded Values see p. 578).

Source.—This remarkable oil is extensively used in China and Japan in the manufacture of varnish and paints, and for rendering fabrics waterproof, but until about 25 years ago was hardly known as a commercial article in Europe.

Although it has frequently been stated that the Japanese and Chinese oils are identical, *Chapman*[1] has shown that Japanese tung oil is derived from a different tree, *Paulownia imperialis*, whereas the Chinese tung oil is the product of *Aleurites cordata*, and possibly of other species of *Aleurites*.

The oils also differ in characteristics, as is shown in the table of values on next page. In the heat test the Japanese oil does not solidify at so low a temperature as the Chinese oil.

Extraction.—According to *Cloez*[2] the nuts, when subjected to cold expression, yield about 35 per cent. of a clear colourless oil, and about 44 per cent. on extraction with carbon bisulphide.

De Negri and *Sburlati*[3] obtained 53·25 per cent. of oil by extraction with solvents, and 43 per cent. by cold expression.

A greater yield is obtained by hot expression, but the oil is brown, has a penetrating and unpleasant odour, and is not so valuable in commerce.

The methods of extraction used in China are still of a very primitive character.[4]

Composition.—Tung oil contains 10·4 to 10·6 per cent. of glycerol, 96 per cent. of insoluble fatty acids, and about 0·5 per cent. of insoluble matter (*Jenkins*).

Cloez[5] found that oil recently extracted by cold expression consisted of 25 per cent. of ordinary olein and 75 per cent. of *elæomargin*. He

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[1] *Analyst*, 1912, xxxvii., 543.

[2] *Comptes Rendus*, 1875, lxxxi., 469.

[3] *Atti della Societa Ligustica di Scienza Nat.*, 1896, vii., [3].

U.S.A. Consular Rep., June 24, 1912.

[5] *Comptes Rendus*, lxxxii., 501.

TUNG OIL.

CHINESE WOOD OIL. JAPANESE WOOD OIL. ELÆOCOCCA OIL. CAY-DEANSON (COCHIN-CHINA).

Recorded Values.

Oil.

Specific Gravity.	Acidity as Oleic Acid.	Saponification Value.	Iodine Value.	Bromine Value.	Solidification Point.	Refractive Index.	Viscosity (Redwood).	Authority.
	Per cent.				° C.	20° C.	15·5° C.	
0·936 at 15° C.	1·18	155·6	159	..	2-3	..	..	De Negri and Sburlati.
0·941 at 15° C.	0·39	172	161	..	..	..	..	De Negri and Sburlati.
0·9405 at 15·5° C.	1·18	191·2	155·7 (*a*)	98	..	..	..	Deering.
0·9343 at 15·5° C.	1·83	192	149·7	..	below — 17	..	..	Jenkins.
0·9385	3·84	194	165·7	..	below — 17	..	..	Jenkins.
0·9413-0·9432	2·85-5·05	190·7 to 196·1	155·4 to 161·8	93·6 to 104·3	..	..	..	Williams (12 samples).
At 15° C. 0·9406-0·9440	..	192·0 to 196·6	166·4 to 176·2	..	..	1·5170 to 1·5207	1,636 to 2,178	Chapman (17 samples Chinese oil).
av. 0·9425	..	av. 194·2	av. 170·6	..	..	av. 1·5179	av. 1,850	
0·9349-0·9400	..	193·4 to 196·3	149 to 158	..	..	1·5034 to 1·5038	1,230 to 1,620	Chapman (3 samples Japanese oil).
0·9365-0·9422	..	189 to 199	156 to 171	..	..	1·5110 to 1·5202	..	Hoepner and Burmeister.
		av. 192	av. 164·6			av. 1·5175		

Fatty Acids.

Melting Point.	Solidification Point.	Saponification Value.	Iodine Value.	Iodine Value of Liquid Fatty Acids	Molecular Equivalent.	Authority.
° C.	° C.					
43·8	31·2	188·8	159·42	..	..	De Negri and Sburlati.
30-31	..	..	144·1	..	..	Jenkins.
37	..	..	150·1	..	..	Jenkins.
40-49·4	37·1-37·2	..	..	..	327·333	Williams (2 samples).
..	..	..	..	178·4-179·7	..	Lane.

termed the fatty acid in this glyceride first *margarolic* and subsequently *elæomargaric acid.* Its formula, according to his elementary analysis, is $C_{17}H_{30}O_2$.

The mixed fatty acids show a characteristic rosette-like appearance on solidification; but on exposure to the air the mass becomes soft and viscous.

Morrell[1] separated a fatty acid, β-elæostearic acid, $C_{18}H_{32}O_2$ (or $C_{18}H_{30}O_2$), from polymerised tung oil. It melted at 72° C., and had an iodine value of 175·4 to 183·5. It yielded a small amount of solid tetrabromide (m.p. 115° C.), but the main bromination product was an oily tetrabromide.

Properties—*Odour.*—The oil extracted by *Cloez* was without odour, but that obtained by *De Negri* and *Sburlati* by cold expression had a peculiar odour, recalling that of castor oil of the second pressing.

The unpleasant smell of the commercial oil has stood in the way of its general use in the linoleum and varnish industries, and although numerous attempts have been made to prevent this, no method giving permanent results has yet been published.

The most successful was that of *Ulzer*[2] who caused steam to be blown through the oil at a temperature of 130° C.; but the oil solidified on cooling. The action of steam at 165° C. caused a marked diminution in the odour after five hours, but after standing for twelve hours the deodorised product yielded a crystalline deposit, and again acquired the characteristic odour of the original oil, though with less intensity than at first. The restoration of the odour was retarded by the exclusion of air.

Specific Gravity.—This is remarkably high, approximating that of boiled linseed oil. The variations in the commercial oil may be attributed partly to the result of oxidation and partly to the oil being obtained from various species of *Aleurites.*

Oxidising Properties.—Tung oil exceeds all other known oils in the readiness with which it undergoes oxidation, but the formation of a solid film, like linoxyn, takes place at a later period than in the case of linseed oil.

Jenkins[3] found that two samples increased in weight at the rate of 0·26 and 0·36 per cent. during each hour when exposed in a shallow basin in a hot water oven.

Williams[4] determined the percentage of oxygen absorbed on exposing about 0·5 gramme of the oil on a watch-glass for several hours at 100° C. The results obtained with 12 samples varied from 4·24 to 7·17 per cent. In his opinion the films compared unfavourably in every respect except rapidity of drying with those yielded by more slowly-drying oils.

Fahrion[5] obtained the following comparative results in the analysis of dried films from linseed and tung oils :—

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[1] *J. Chem. Soc.*, 1912, ci., 2082.

[2] *J. Soc. Chem. Ind.*, 1901, xx., 261.

[3] *Analyst*, 1898, xxiii., 113.

[4] *J. Soc. Chem. Ind.*, 1898, xvii., 304.

[5] *Farben Zeit.*, 1912, xvii., 2530.

	Fatty Acids.	Melting Point of Fatty Acids.	Iodine Value of Fatty Acids.	Hydroxy Acid Solution in Ether.	Hydroxy Acid Solution in Alcohol.	Iodine Value.	Hehner Value.
	Per cent.			Per cent.	Per cent.		
Linoxyn, .	25·3	38	42·9	40·2	20·2	28·3	85·7
Tungoxyn, .	11·2	40	47·6	70·6	..	26·2	81·8

The dry film from tung oil was white, firm, only slightly elastic, and free from stickiness.

Owing to its drying properties tung oil can be used without preliminary oxidation for varnishes. It is also employed for rendering paper water-proof, and paper thus treated is transparent and can be written on with ordinary ink.

Polymerisation on Heating.—*Cloez* found that when the oil which had been extracted with carbon bisulphide was exposed to the light in the absence of air it became solid, and he established the fact that this solidified mass had the same composition as the original oil. It had a crystalline structure, melted at 34° C. and solidified at 32° C.

On saponifying this polymerised oil *Cloez* obtained a mixture of solid fatty acids, which, on repeated crystallisation from alcohol, yielded an acid (melting at 72° C.), to which he gave the name of *stearolic* or elæostearic acid.

This was confirmed by *De Negri* and *Sburlati*, who found that by boiling the flour from the nuts with water, an oily liquid separated out. This had an iodine value of 147·8 and a saponification value of 162·5. After standing for twenty-four hours it solidified, and the iodine and saponification values of the product were 144·5 and 153·3 respectively.

Jenkins (*loc. cit.*) has further studied this polymerising property. The oil, after being heated for two hours at 200° C. out of contact with the air, still remained liquid. The temperature was then raised to 250° C., and after another two hours the oil thickened and yielded in one case a sticky elastic jelly, and in the other a hard, dry, elastic mass.

Heat Test.—*Browne*[1] suggests the following standard method of applying the heat test:—Five c.c. of the oil are placed in a test-tube (16 cm. by 15 mm.), through the cork of which a glass rod can be moved up and down. This tube is placed in a bath of cotton-seed oil of standard dimensions, previously heated to 560° C. The time is noted, the source of heat removed for 45 seconds and then re-applied, so that the temperature of the bath is maintained at 282° C. After nine minutes from the introduction of the tube the glass rod is raised at intervals of 30 seconds, and the time noted when the oil has set to a firm jelly. Seven samples of wood oil gave values of 11 to 13 minutes, whilst samples containing 10 to 20 per cent. of other oils gave values of 13 to 19 minutes.

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[1] *Chem. News*, 1912, cvi., 14.

Bacon's Test.—About 10 c.c. of pure tung oil are placed in a test-tube ¾ inch in diameter and about 4 inches long, and similar tubes are charged with the same oil adulterated to the extent of 10 per cent., and with the sample under examination. The three tubes are immersed for exactly nine minutes in an oil-bath at 280° to 285°. The contents of each are then stabbed with a small bright spatula. In the case of pure tung oil the cut will be clear and appear as a straight line, whilst oils containing 5 to 10 per cent. of adulterant will show soft, feathery appearance, or be more or less liquid.[1]

Iodine accelerates the polymerisation (*vide infra*). In *Boughton's*[2] test 10 c.c. of the oil and 10 c.c. of a saturated solution of iodine in chloroform are heated in the water-bath until the solvent has evaporated, and then at 200° C. for an hour in an oil-bath. The presence of 10 per cent. of tung oil causes linseed oil to solidify.

Tung oil polymerised by light finds a use in commerce as a means of preventing the separation of the metallic pigment from the oil in oil paints in tubes. The addition of about 10 per cent. of the product gives satisfactory results, and also accelerates the drying of the paint.

Solidifying Point.—The freshly-expressed oil congeals at + 2° to 3° C., but only after the cooling has been continued for at least four hours. The solidification point is lowered on keeping. Thus, *De Negri* and *Sburlati* found that oil obtained from the same nuts by cold expression only began to solidify at − 18° C. after it had been kept for six months.

Cloez observed that tung oil could be cooled to − 18° C. without losing its transparency, and *Jenkins* noticed the same fact in the case of two specimens of the oil.

Optical Properties.—*Jenkins* found a specimen of tung oil to have a refractive index of 1·503 at 19° C., with sodium light. It had no action on polarised light.

Chinese wood oil has an anomalous optical dispersion, the spectrum showing blue and green on the top, with red on the lower side; whilst in the case of other oils the spectrum has red on the upper side and green and blue on the lower. On adding other oils to tung oil, it has been shown by *Brier*[3] that the "turning point" of the spectrum varies within the limits of 14·5 and 17 per cent., but if the definite adulterant be known, its quantity may be calculated within about 1·25 per cent.

Action of Bromine and Iodine.—Tung oil apparently forms one of the exceptions to the general rule that the heat of bromination is proportional to the iodine value, though this may not be the case with the absolutely fresh oil.

With a vacuum tube with which the bromine thermal factor was 5·7 for ordinary oils, it was necessary to use the factor 7 (*Jenkins*).

The present writer (*M.*) examined the same specimen of oil three years afterwards with a similar result.

In the table of recorded values Hübl's method was used by *Hoepner*

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[1] Calef, *Oil, Paint, and Drug Rep.*, 1912, 19.

[2] *Analyst*, 1909, xxxiv., 362

[3] *J. Ind. Eng. Chem.*, 1915, vii., 953.

and *Burmeister*,[1] as they were unable to obtain trustworthy results by the methods of Wijs and Hanus.

Rowland Williams [2] has shown that there is a considerable difference between the bromine and iodine values of tung oil, whereas in the case of many oils it matters but little which value is determined. He gives the following results :—

Iodine Value (*Wijs*).	Bromine Value calculated from Iodine Value.	Bromine Value (*M'Ilhiney*).	Bromine Addition.	Bromine Substitution.
158·42	100·12	95·83	92·33	1·75

A solution of iodine in chloroform, or other solvent, converts the oil into a jelly-like mass (*Jenkins*).

Williams obtained bromine values of 93·57 to 104·30 with 12 specimens of oil by Hehner's gravimetric method.

Sulphur Chloride Test.—*Jenkins* [3] found that 5 grammes of the oil stirred for 1½ minutes with 2 c.c. of carbon bisulphide and 2 c.c. of sulphur chloride suddenly yielded a thick jelly. The mass was not so hard as that obtained from linseed or castor oils.

Free Fatty Acid.—In the freshly-expressed oil this is as low as 0·39 (*De Negri* and *Sburlati*), but in the commercial oil it varies from 3 to 5 per cent. as oleic acid. According to *Lippert* [4] this large proportion of acid causes the oil to thicken with inconvenient rapidity in the presence of oxide pigments.

Viscosity.—The two specimens examined by *Jenkins* required (1) 858 and (2) 1,433 seconds for 50 c.c. to flow from Redwood's viscosimeter at 60° F. The same volume of water took 28 seconds, and pure rape-seed oil an average of 470 seconds. *Jenkins* suggested that the great difference in the two results might be due to partial polymerisation of the second sample.

Solubility in Different Solvents.—Tung oil dissolves in ether, petroleum spirit, chloroform, and carbon tetrachloride, but is insoluble in cold absolute alcohol.

It dissolves in an equal volume of boiling glacial acetic acid, but the solution becomes turbid at 95° C. (*De Negri* and *Sburlati*).

The two specimens examined by *Jenkins*, however, gave Valenta figures of 47° and 44° C. respectively.

Elaidin Reaction.—According to *Jenkins* the oil darkens considerably, and separates into an oily upper layer and more solid lower layer.

Maumené Test.—On treatment with sulphuric acid, tung oil instantly solidifies to a black charred mass. By diluting it with olive oil, and making an allowance for the addition, *Jenkins* obtained specific temperature reactions of 298° and 330° with his two samples.

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[1] *Chem. Zeit.*, 1913, xxxvii., 18, 39.

[2] *J. Soc. Chem. Ind.*, 1900, xix., 300.

[3] *Ibid.*, 1897, xvi., 195.

[4] *Zeit. angew. Chem.*, 1897, 779

As is the case with the bromine thermal value, the "Halogen Standard Maumené Figure" (*q.v.*) does not appear to stand in any definite relationship to the iodine value of either the oil or the fatty acids.

Standards of Purity.—The New York Produce Exchange has adopted the following standard for Chinese wood oil :—

> "Prime Chinese wood oil shall be pale in colour (according to the season's production), merchantably free from foots, dirt, and moisture ; the total impurities shall not exceed 1 per cent., but impurities up to 5 per cent., not plainly adulterations, shall not justify rejection ; but allowance shall be made by the sellers for such impurities in excess of 1 per cent." [1]

The oil must satisfy the requirements of the Bacon test or a similar test devised by Worstall.

Colour Reactions—Becchi's Test.—One of Jenkins' samples gave a brown colour resembling that given by cotton-seed oil, whilst the other did not darken to any appreciable extent after being heated for fifteen minutes.

Baudouin's and *Halphen's* reagents produce no colorations.

WALNUT OIL (NUT OIL).

Recorded Values.

Walnut Oil.

Specific Gravity.	Acidity as Oleic Acid.	Saponification Value.	Iodine Value.	Hehner Value.	Refractive Index.	Authority.
	Per cent.					
0·9250-0·9268 at 15·5° C.	..	194-197	143-146	..	..	De Negri & Fabris.
0·9215 at 15° C.	8·6-9	190·1-191·5	141·4-142·7	93·77	..	Kebler.
..	..	..	142·8	..	..	Mitchell.
0·924 at 15° C.	..	..	..	..	..	Bishop.
0·9224 at 24° C.	..	..	138·84	..	1·4770	Merrill.
					Oleo-refractometer.	
0·9260 hot-pressed 0·9250 cold- „	..	196-197	142-143	..	..	Andés.
0·9258 at 15° C.	4·38	..	148·21	..	67·7° at 40° C.	Petkow,[2] mean of 5 cold-expressed.
0·9259	2·53	192·5	143·1	95·44	1·4689	Crossley & Le Sueur (Indian).
0·926	..	192·1	128	..	..	Shukoff (Russian).
..	..	191·6	150·2	..	..	Lane.
0·9184	..	198·0	106 (Hübl)	93·4	..	Deiler and Traps[3] (extracted oil).

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[1] Trade Report, *Oil, Paint, and Drug Rep.*, Sept. 23, 1912.

[2] *Chem. Rev. Fett Ind.*, 1901, viii., 209.

[3] *Amer. Chem. J.*, 1910, xliii., 90.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
°C.			
15-20	..	150·05	De Negri and Fabris.
20	16	..	Andés.
0	..	..	Kebler.
	Dalican's Test.	Liquid Acids.	
..	14·3	..	Shukoff.
..	..	146 (rancid)	Lane.
..	..	167 (fresh)	„

Source.—Walnut oil is obtained from the kernels of the walnut (*Juglans regia*), which contain from 63 to 65 per cent. *Kebler*[1] obtained by cold expression of the crushed kernels 25 per cent. of oil, the total amount present being about 66 per cent.

The cold-pressed oil, when fresh, is occasionally used as an edible oil, but the hot-pressed oil has a sharp and disagreeable flavour. It soon becomes rancid, and is then said to have a purgative effect.

It is also employed as a lamp oil, but its chief use is as a medium for white paint, for which its pale colour renders it more suitable than linseed oil. According to Kebler, it is very extensively adulterated in America.

Composition.—Walnut oil has been found to contain myristic and lauric acids, and the liquid fatty acids, according to *Hazura* and *Grüssner*, consist of oleic acid, 7 per cent.; linolic acid, 80 per cent.; and linolenic and isolinolenic acids, 13 per cent.

An ethereal solution of the oil yielded from 1·5 to 1·9 per cent. of an insoluble bromide, containing 58·58 per cent. of a bromide (*Hehner* and *Mitchell*[2]). This compound is evidently a mixed glyceride analogous to that obtained in much larger proportion from linseed oil.

Fouchet[3] found an oil obtained from the seeds of a cross between *Juglans niger* and *J. cinerea* to have an iodine value of 151, and to contain about 70 per cent. of linolic acid, together with oleic, linolenic, and stearic acids.

Properties.—The cold-expressed oil is limpid and of a pale straw colour, but that obtained by hot expression is much darker, and has a peculiar taste and smell. It dissolves in 60 times its volume of boiling alcohol.

Solidification Point.—According to *Kebler*, walnut oil solidifies at — 12° C., whilst *De Negri* and *Fabris* give the solidification point as — 15° to — 28° C., and *Andés* at — 17° to — 24° C.

The melting point of the fatty acids, as given by *Kebler*, is very

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[1] *Amer. J. Pharm.*, 1901, lxxiii., 173.

[2] *Analyst*, 1898, xxiii., 315.

[3] *Bull. Sci. Pharm. acol.*, 1912, xviii., 529.

different from that found by *De Negri* and *Fabris*, but this is possibly due to the oil examined by the former having been obtained by cold expression, and thus containing less of the solid glycerides.

Oxidation.—Walnut oil, on drying, yields a thin transparent film, which is said to be less liable to crack than the film from linseed oil.

It dries somewhat less rapidly, however, and takes up less oxygen. *Bishop*[1] gives the mean amount of oxygen absorbed as 13·70 per cent. as compared with linseed oil absorbing 15 to 17·7 per cent.

Maumené Test.—*De Negri* and *Fabris* found this to vary from 96° to 101° C. by Maumené's original method.

Heat of Combustion.—*Merrill*[2] obtained 9,438 calories per gramme with a specimen of oil.

Colour Reactions.—Walnut oil gives no coloration with *Becchi's* or *Milliau's* reagents.

Viscosity.—*Crossley* and *Le Sueur* found walnut oil to have a viscosity of 9·13 compared with water at 70° F. as unity.

Detection of Linseed Oil.—The percentage of linolenic acid in the mixed fatty acids of walnut oil is too small to yield any precipitate of linolenic hexabromide on treatment with bromine, so that in cases of mixtures of linseed oil and walnut oil an approximate estimation of the amount of the former may often be obtained by Hehner and Mitchell's method, reckoning unoxidised linseed oil fatty acids to yield from 21 to 23 per cent. of insoluble bromide. A better method is to determine the amount of the insoluble bromide yielded by the oil itself, as in the following determinations made by *Hehner* and *Mitchell*.[3]

Oil.	Linseed.	Insoluble Bromide.	Linseed Oil, Calculated from Bromide.
	Per cent.	Per cent.	
Linseed, ...	100	23·86	100
Linseed and walnut, .	69	16·6	69
,, ,, ,, .	38·2	9·3	38·1

Of course this test would not be trustworthy in the case of boiled oil, which, as *Hehner* and *Mitchell* have shown, does not yield insoluble bromide to any appreciable extent.

Walnut oil is sometimes also adulterated with sesamé and earthnut oils, and with rosin oils, and is itself used as an adulterant for olive oil. Modifications of Hehner and Mitchell's insoluble bromide method (pp. 562-565) should give useful information in the latter case when considered in conjunction with the iodine value and other constants.

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[1] *J. Pharm. Chim.*, 1896, vii., 55.

[2] *Maine Agric. Exp. Stat. Bull.*, 1900, [65], 111.

[3] *Analyst*, 1898, xxiii., 316.

CLASS VII.—TRAIN, LIVER, AND FISH OILS.

COD-LIVER OIL.

Recorded Values.

Cod-liver Oil.

	Specific Gravity.	Hehner Value.	Saponification Value.	Iodine Value.	Maumené Test.	Solidification Point.	Authority.
					°C.	°C.	
Commercial,	0·923-0·730 at 15° C.	...	182-187	...	113	...	Allen.
,,	...	...	185·1-188·2	158 7-166·6	243-272 Sp. Temp. Reaction.	...	Thomson and Ballantyne.
...	...	95·3	...	141-143·4	...	...	Lewkowitsch.
...	0·927	...	...	147	...	...	Fahrion.
...	0·922-0·927	...	171-189	123-141	...	.	Kremel.
"Cod oil,"	0·9227	.	173·6	137·5	...	-3	Mitchell.
Fresh oil,	0·9270	...	...	165·6	...	...	Sherman and Snell.
Old oil,	0·935	...	...	137·3	..	...	,,
Japanese oil,	0·9272	....	184·7	140·8	...	...	Bull.
Lofoden oil (white),	0·9232	...	183 7	144·6	...	...	,,
Brown cod oil (Hamburg),	0·9310	...	175·2	147·9	...	...	,,

Fatty Acids.

	Specific Gravity at 60° C.	Melting Point.	Solidification Point.	Iodine Value.	Refractive Index at 60° C.	Authority.
		°C.	°C.			
Medicinal and commercial,	...	48-51	...	...	...	Kremel.
			Dalican's Test.			
Medicinal, .	...	...	17·5-18·4	...	...	Lewkowitsch.
Crude, . . .	...	...	22·5-24·3	...	...	,,
"Cod oil," .	...	21·8	17·4	124·3	...	Mitchell.
Medicinal, .	0·882-0·900	...	...	...	1·4578-1·4645	Procter.

Source.—Cod-liver oil is, as its name denotes, obtained from the liver of the cod fish, *Gadus morrhua*, being separated by the methods described in Chap. x.

For pale medicinal oil the livers are treated in as fresh a condition as possible, the dark brown products, "cod oil," being separated from the livers that have undergone more or less decomposition (see Chap. x.).

Oils of different origin differ in the amount of solid deposit obtained on exposure to cold. Thus *Jorissen*[1] found that the majority of commercial oils examined by him remained fluid, while some became nearly solid.

Composition—*Fatty Acids.*—Cod-liver oil has been shown to contain the glycerides of stearic, palmitic, and lower saturated fatty acids (*vide infra*).

There is considerable doubt as to the nature of the unsaturated fatty acids, and many of the statements that have been made require confirmation.

Fahrion[2] found jecoric acid, $C_{18}H_{30}O_2$, an isomer of linolenic acid in sardine oil, but was unable to identify it in cod-liver oil.

Hehner and *Mitchell*,[3] however, separated an insoluble bromide from the mixed fatty acids, which resembled linolenic hexabromide in containing 62·91 per cent. of bromine as against the theoretical quantity 63·31 per cent., but differed from it in decomposing below 200° C., before its melting point was reached.

Cod-liver oil also resembles linseed oil (*q.v.*) in yielding a large amount (42 per cent. in one case) of a white solid bromide containing 56·32 per cent. of bromine. This, too, decomposes before its melting point is reached.

Möller[4] has isolated a still more unsaturated acid, of the series $C_nH_{2n-8}O_2$, and his statement receives confirmation from the experiments of *Bull*,[5] who separated fatty acids of the series $C_nH_{2n-10}O_2$ by treatment of the mixed sodium salts with ether. This was probably the same acid as the clupanodonic acid isolated from Japanese sardine oil by *Tsujimoto*.[6]

Bull also found erucic acid, $C_{22}H_{42}O_2$, and a new acid of the oleic series, $C_{21}H_{40}O_2$. This melted at 24·5° C., had an acid value of 171·6, and yielded a lead salt readily soluble in ether. The unsaturated acids, separated as described on p. 159, had iodine values as high as 341·8. Myristic, palmitic, and stearic acids have also been identified.[7]

Unsaponifiable Matter.—This consists principally of cholesterol, which can be separated by the methods described in Chap. vi.

The following quantities of cholesterol have been separated from oils of various origin by different chemists:—Medicinal oil, 0·54 to 1·44 (*Fahrion*); commercial oil, 0·65 to 2·62 (*Fahrion*), 0·6 to 0·78

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[1] *Chem. Zeit.* (Rep.), 1896, xx., 103.
[2] *J. Soc. Chem. Ind.*, 1893, xii., 935.
[3] *Analyst*, 1898, xxiii., 317.
[4] *Cod-liver Oil and Chemistry.*
[5] *Chem. Zeit.*, 1899, xxiii., 1043.
[6] *J. Coll. Eng. Tokyo*, 1906, iv., 1.
[7] *Ber.*, 1906, 3570.

(*Lewkowitsch*); brown cod oil, 1·82 to 2·68 (*Fahrion*), 1·87 (*Thomson* and *Ballantyne*).

Organic Nitrogenous Bases.—The medicinal effects of cod-liver oil are probably due, to some extent, to the presence of various nitrogenous bases (*leucomaines*), which, according to *Gautier*, are present to the extent of about 0·05 per cent.

The following are the principal bases that have been described :—

Amylamine,	$C_5H_{11}.NH_2$
Hexylamine,	$C_6H_{13}.NH_2$
Dihydrolutidine,	$C_7H_{11}N$
Merlusine,	$C_8H_{12}N_2$
Morrhuine,	$C_{19}H_{27}N_3$
Homo-morrhuine,	$C_{20}H_{29}N_3$
Nico-morrhuine,	$C_{20}H_{28}N_4$
Aselline,	$C_{25}H_{32}N_4$
Tyrosamines,	C_7H_9NO ; $C_8H_{11}NO$; $C_9H_{13}NO$
Morrhuamine,	$C_{14}H_{20}N_2O_2$

Gautier[1] found two-thirds of the bases in a sample of cod-liver oil to consist of an amylamine, whilst in another specimen more than a third consisted of morrhuine and homo-morrhuine, and a fifteenth part of aselline. Doubtless the presence of many of the bases in the preceding list was due to putrefactive changes in the livers prior to the extraction of the oil.

Inorganic Substances.—In addition to phosphorus, iron, manganese, magnesium, calcium, and sodium have been identified in cod-liver oil. The proportion of iodine varies from a slight trace to 0·031 per cent. (*Andrés*).

Free Fatty Acids.—When obtained from absolutely fresh livers, cod-liver oil contains only traces of free fatty acids, but owing to the readiness with which the oil changes on keeping they soon develop, and in the oil extracted from decomposed livers they reach a high proportion. Thus *Thomson* and *Ballantyne* found a sample of medicinal oil to contain 0·36 per cent. of free acids (as oleic acid), whilst a sample of brown "cod oil" contained 23·31 per cent.

Sherman and *Snell*[2] found 0·56 per cent. of free acid in fresh oil and 1·50 per cent. in old oil.

Properties and Tests of Purity—*Specific Gravity.*—This ranges from about 0·922 to 0·930, at 15° C. The oil from other marine animals has about the same density.

Allen[3] gives the following table of the specific gravity of various oils of this class :—

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[1] *Les Toxines*, 76.

[2] *J. Amer. Chem. Soc.*, 1901, xxiii., 164.

[3] *Commercial Organic Analysis*, 1899, ii., [1], p. 31.

Oil.	Specific Gravity at 15·5° C.
Cod-liver, ...	0·929
Hake-liver, ...	0·927
Skate-liver, ...	0·9327
Shark-liver, ...	0·9285
Mixed liver oils, from cod, haddock, ling, whiting,	0·930
Haddock-liver (Aberdeen), ...	0·931
Ray-liver, ...	0·928
Herring oil, ...	0·9326
Sprat oil, ...	0·9284
Seal oil, ...	0·9245
Whale oil, ...	0·9301

Bromine and Iodine Values.—The action of bromine is considerably more complete than that of iodine, judging by the following results obtained by *Vulté* and *Logan*[1]:—

Iodine Value (*Hübl*).	Iodine Value Calculated from Bromine.	Total Bromine Absorption.	Bromine Addition Value.	Bromine Substitution Value.
122·1-122·8	132·9-132·2	84·91	84·3	0·60

It is possible, however, that the action of the iodine was not allowed to continue for a sufficient length of time.

Acetyl Value.—*Lewkowitsch*[2] obtained an acetyl value of 1·15 with fresh cod-liver oil, whilst a sample which had been kept for some years showed a value of 5·8.

Reichert Value.—Oil prepared from perfectly fresh livers is practically free from volatile fatty acids. According to *Salkowski*,[3] this value should not exceed 0·20.

Refractive Index.—*Procter* has obtained results varying from 1·481 to 1·482 with different kinds of oil, and 1·4865 with a specimen of blown cod-liver oil.

Dowzard[4] advocates the use of Amagat and Jean's oleo-refractometer as a certain means of detecting seal oil. He found that pure

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[1] *J. Amer. Chem. Soc.*, 1901, xxiii., 156.

[2] *Analyst*, 1899, xxiv., 319.

[3] *J. Soc. Chem. Ind.*, 1898, xvii., 1023.

[4] *Pharm. J.*, 1898, 532.

cod-liver oil, of different origin, after being shaken with alcohol (sp. gr. 0·800) heated to 30° C., separated and dried at 110° C., gave results ranging from + 44 to + 45, whilst in two doubtful cases readings of + 43·5 were obtained. In the case of three specimens of seal oil, the reading varied from 32 to 32·5. A mixture of cod-liver and seal oils gave the following readings at 22° C. :—

Cod-Liver Oil.	Seal Oil.	Refractometer Reading at 22° C.
Per cent.	Per cent.	
100	0	+ 44·50
90	10	+ 43·25
80	20	+ 42·0
70	30	+ 40·75
60	40	+ 39·50
50	50	+ 38·25
40	60	+ 37·00
30	70	+ 35·75
20	80	+ 34·50
10	90	+ 33·25
0	100	+ 32·0

Eight specimens of cod-liver oil examined by *Pearmain*[1] with this instrument gave readings ranging from + 40 to + 46, the average being + 44; whilst seal oil gave readings averaging + 33.

Heat of Combustion.—The following results were obtained by *Sherman* and *Snell*,[2] 9,437 calories per gramme (constant volume) for fresh oil, and 9,277 calories for old oil.

Maumené Test.—Owing to the presence of so large a proportion of unsaturated fatty acids, great heat is liberated on treating cod-liver oil with sulphuric acid. In the older methods of applying the Maumené test the following values have been obtained:—102 to 103 (*Maumené*); 113 (*Allen*); 116 (*Baynes*); specific temperature reaction, 243 to 272 (*Thomson* and *Ballantyne*). *Mitchell*[3] has shown that the *halogen standard figure* of the fatty acids is proportional to their iodine value.

Drying Properties.—Cod-liver oil absorbs a considerable amount of oxygen on exposure to the air, and becomes thicker though without drying. Hence the presence of any notable quantity of linseed oil would be indicated by the film test, but not by Livache's or Fahrion's tests.

Colour Reactions—*Salkowski's Cholesterol Reaction.*—A solution of cholesterol in chloroform, when shaken with an equal proportion of sulphuric acid, gives a blood-red colour, changing to lighter red and finally to purple. If a few drops of this purple chloroform layer be

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[1] *Analyst*, 1895, xx., 135.

[2] *J. Amer. Chem. Soc.*, 1901, xxiii., 164.

[1] *Analyst*, 1901, xxvi., 169.

placed on porcelain, the colour passes through blue and green to yellow.

On testing cod-liver oil in this way, a violet-blue colour is produced, which gradually changes to brown. In *Salkowski's* opinion a lipochrome and the fatty acids contribute to this reaction.

German Pharmacopœia Test.—One drop of pure cod-liver oil dissolved in 20 drops of carbon bisulphide, and mixed with one drop of strong sulphuric acid, should give an immediate violet coloration, changing afterwards to red and then brown. This coloration is also obtained with other liver oils (*Lewkowitsch*), whilst old or rancid oils give a red coloration.

Other Colour Tests.—*Tozelli*[1] recommended the following reagents for the detection of fish and seal oil in cod-liver oil:—A, 1 part of concentrated sulphuric acid to 20 parts of oil; B, 10 parts of sulphuric acid to 20 of oil; C, 1 part of concentrated nitric acid to 20 parts of oil; D, 15 parts of solid litmus to 20 of oil.

He obtained the subjoined results:—

Oil.	A.	B.	C.	D.
Pure cod-liver oil,	Violet colour, changing to red-brown.	Soap-like mass after two to three hours.	Rose to orange-red colour.	Remained blue for at least one hour.
Cod-liver oil with much fish oil,	Reddish-brown.	Consistency of vaseline after two hours.	Red, changing to brown.	Changed to red within one hour.
Cod-liver oil with much seal oil,	Cochineal red.	Consistency of soft extract after one hour.	No colour, but consistency as in B.	Consistency as in B and C.

Gawalowski (*loc. cit.*) finds that these reactions are not applicable to every variety of cod-liver oil, and that the litmus test is unreliable.

In *Lewkowitsch's* experience, colour reactions with nitric and sulphuric acids cannot be relied upon as tests of purity.

Chapman[2] describes the differences between the colour reactions of cod-liver oil and shark-liver oil containing spinacene.

Detection of Adulteration.—In addition to *seal oil* and *fish oils*, various *vegetable oils*, *mineral oils*, and *resin oils* have been used to adulterate cod-liver oil.

Vegetable Oils.—Drying oils can be detected by a modification of Hehner and Mitchell's bromide test (p. 568); whilst non-drying vegetable oils are indicated by the reduced iodine value and Maumené figure. The phytosterol tests would probably also afford valuable information.

Mineral and Resin Oils.—The best test for these is the determination of the amount and nature of the unsaponifiable matter.

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[1] *J. Soc. Chem. Ind.*, 1898, xvii., 607.

[2] *Analyst*, 1917, xlii., 161.

DOLPHIN OIL.

Recorded Values.

Dolphin Oil.

Origin.	Specific Gravity at 15° C.	Saponification Value.	Reichert Value	Hehner Value.	Iodine Value.	Solidification Point.	Authority.
Body oil, .	0·9180	...	...	...	...	yields deposit at 5° to −3° C.	Schädler.
,, .	...	197·3	5·6	93·1	99·5	...	Moore.
Jaw oil, .	...	290	65·92	66·28	32·8	...	,,

This oil is contained in the blubber of the dolphin, *Delphinus globiceps*, from which it is separated in the same manner as whale oil.

It consists mainly of glycerides of various acids, but also contains esters of other alcohols, and on standing yields a deposit of spermaceti.

There is a marked difference in the characteristics of the oil from the body and from the jaw of the dolphin, as is seen in the results obtained by *Moore*[1] (*vide supra*). The jaw oil, which is used as a lubricant, contains a remarkably high percentage of glycerides of volatile fatty acids.

MENHADEN OIL.

Recorded Values.

Menhaden Oil.

Specific Gravity.	Saponification Value.	Reichert Value.	Iodine Value.	Maumené Test.	Solidification Point.	Authority.
				° C.	° C.	
0·927 -0·933	192	1·2	148-160	126	...	Allen.
...	...	...	147·9	123-128	..	Archbutt.
				Specific Temp. Reaction.		
0·931	189·3	...	160	306	...	Thomson & Ballantyne.
0·931	189	...	160-180	...	...	M'Ilhiney.
0·925 -0·930	...	...	...	...	...	Schädler.
0·9235-0·925	...	...	...	...	−4	Jean.

Menhaden or American fish oil is obtained from the menhaden, *Alosa menhaden*, a fish caught near the coast of North America.

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[1] *J. Soc Chem. Ind.*, 1890, ix., 331.

The oil (about 15 per cent. of the fish) is separated either by boiling the material in pans with false bottoms, or by a continuous process of steaming. After separation of the oil the residual "fish scrap" is expressed in hydraulic presses to obtain a lower grade of oil, and the press-cake ("chum") is dried and used as manure.

According to *Jean*,[1] it contains about 0·02 per cent. of iodine.

The amount of unsaponifiable matter found by *Fahrion* in different samples of the oil, ranged from 0·61 to 1·43. The addition of mineral oil would be indicated by an increase in this constituent.

Menhaden oil is chiefly employed in the manufacture of dégras and as a currying oil (*Jean*).

According to *M'Ilhiney*, it is used as an adulterant of linseed oil (see *Linseed Oil*).

PORPOISE OIL.

Recorded Values.

Porpoise Oil.

Origin.	Specific Gravity.	Saponification Value.	Iodine Value.	Hehner Value.	Reichert Value.	Maumené Test.	Authority.
						°C.	
Jaw oil, strained,	...	253·7	49·6	72·05	47·77	...	Moore.[2]
,, ,,	...	272·3	30·9	68·41	56·0	...	,,
,, not ,,	...	143·9	76·8	96·5	2·08	...	,,
Body, . .	...	...	...	...	46·9 (*a*)	...	Steenbuch.[3]
Jaw, . . .	...	...	...	...	131·6 (*a*)	...	,,
...	0·926 at $\frac{15·5° C.}{15·5° C.}$	...	...	...	11-12	50	Allen.
Body oil, .	0·9266 at 15° C.	203·4	126 9	...	...	...	Bull.

(*a*) Reichert-Meissl value.

This oil is obtained from the body or from the jaw only of the porpoise, *Delphinus phocœna*, and is separated by filtration from the more solid portion that deposits on chilling the fat. It is used as a lubricant for fine machinery (*Moore*).

The presence of valeric acid in this oil was first recognised by *Chevreul*. Its proportion was found by *Steenbuch* to be about 10 per cent. of the total soluble fatty acids of the body oil, and 26·8 per cent. in the case of the jaw oil.

Bull[4] separated 14·3 per cent. of highly unsaturated fatty acids with an iodine value of 285·4. The same specimen of oil contained 2·01 per cent. of unsaponifiable matter.

Porpoise jaw oil is soluble in alcohol at 70° C. (*Chevreul*, *Steenbuch*).

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[1] *Chimie des Matières Grasses*, 261.

[2] *J. Soc. Chem. Ind.*, 1890, ix., 331.

[3] *Zeit. angew. Chem.*, 1889, 65.

[4] *Chem. Zeit.*, 1899, xxiii., 1043.

SARDINE OIL.

Recorded Values.

Sardine Oil.

Specific Gravity at 15° C.	Acid Value.	Saponification Value.	Hehner Value.	Iodine Value.	Melting Point.	Solidification Point of Fatty Acids.	Authority.
					° C.	° C.	
0·933	20·6	...	94·5	193·2	...	...	Fahrion.[1]
...	...	190·9-193·8	...	191·7	...	...	,,
			Japanese Fish.				
0·9283	2·2	189·0	...	134·1	...	...	Bull.[2]
...	...	...	...	...	24	30-31	Villon.
...	...	189·8-192·1	...	121·5	...	27·6-28·2	Lewkowitsch.

This fat is obtained from sardines (*Clupea pilchardus*, *C. scombrina*) and is used in the manufacture of dégras and soap, and as a lubricant.

According to *Villon*,[3] it is prepared in Japan by boiling the fish with water or by leaving them to decompose and expressing the mass. The crude oil is refined in Yokohama by being heated in iron boilers, and then transferred to wooden vats, where it separates into three layers—the uppermost consisting of an oil, the middle of a solid fat, and the lowest of water containing albuminous substances in suspension.

The solid fat is melted, filtered, and sold under the name of "fish stearine" or "fish wax."

Villon states that the oil contains 28 per cent. of solid fatty acids and 72 per cent. of liquid fatty acids, and that, as sold, it has the following composition:—Water, 5·52; olein, 57·18; palmitin and stearin, 35·11; free oleic acid, 1·50; iodine, 0·1; and organic débris, 0·2 per cent.

Japanese sardine oil differs considerably from the European oil, as is shown in the table of values, where the iodine value is seen to be considerably lower.

Fahrion (*loc cit.*), by extracting the barium salts of the fatty acids of European oil with ether and liberating the fatty acids from the soluble salts, obtained a liquid fatty acid isomeric with linolenic acid, $C_{18}H_{30}O_2$, to which he gave the name *jecoric acid.*

The only solid fatty acid identified was palmitic acid (13·6 per cent.), and this specimen of oil was therefore calculated to consist of 14·3 per cent. of tripalmitin and 85·7 per cent. of trijecorin.

Jecoric acid was not found in a sample of Japanese oil examined by *Fahrion*. *Bull* (*loc. cit.*), however, separated from Japanese oil 13 per cent. of highly unsaturated fatty acids, which had an iodine value of 319·5, and were thus more unsaturated than Fahrion's jecoric acid.

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[1] *Ibid.*, 1893, xvii., 938.

[2] *Ibid.*, 1899, xxiii., 1043.

[3] *Les Corps Gras Ind.*, 1887, xiii., 178, 196.

SEAL OIL.

Recorded Values.

Seal Oil.

Specific Gravity.	Saponification Value.	Hehner Value.	Reichert Value.	Iodine Value.	Maumené Test.	Oleo-refractometer.	Refractive Index.	Solidification Point.	Authority
0·9155-0·926 at 15° C.	..	...	...	125-130	° C. ...	...	...	deposit at 3° C.	Schädler.
0·924 -0·929 at 15·5° C.	...	...	...	...	92	...	...	...	Allen.
0·9249-0·9263	190·7 to 196·2	92·8 to 94·2	0·07 to 0·22	129·5 to 141	...	...	...	...	Chapman and Rolfe.
0·9244-0·9261	189·3 to 192·8	...	...	142·2 to 152·4	Specific Temp. Reaction. 212-229	...	...	...	Thomson and Ballantyne.
0·9266 at 15° C.	190·6	...	...	143·4	...	...	...	...	Bull.
...	190·7 to 192·9	95·96	...	146·2	...	...	...	...	Fahrion.
0·9249 at 15° C.	...	...	...	...	...	...	1·4784 at 15° C.	...	Procter.
0·8987 at 60° C.	...	...	...	...	...	...	1·4619 at 60° C.	...	,,
...	...	...	...	..	...	30-36	...	...	Pearmain.

Fatty Acids.

Melting Point.	Solidification Point.	Saponification Value.	Molecular Equivalent.	Oxidised Fatty Acids.	Authority.
° C. 22-23	° C. ...	190·4-196	...	Per cent. ...	Chapman and Rolfe.
...	...	...	286·7	0 75	Fahrion.
...	Dalican's Test. 15·5-15 9	...	...	...	Lewkowitsch.

Fahrion found from 0·62 to 1·44 per cent. of unsaponifiable matter and 0·5 to 0·7 per cent. of oxidised acids in different samples of both kinds of oil.

On exposure to the air, sardine oil becomes viscid and resin-like, but does not dry. A sample exposed by *Fahrion* for three weeks showed a great decrease in its iodine value (61·3), whilst its acid value had increased to 53·1.

Sardine oil is not completely soluble in absolute alcohol (*Villon*).

SEAL OIL (for Recorded Values see p. 595).

Origin.—Seal oil is the fat rendered from the blubber of different varieties of seal, *Phoca grœnlandica*, etc. It is exported in a crude state from Greenland to Denmark, where it undergoes a further refining process.

It is sold in three qualities known as "light brown," "brown," and "three crown" seal oil, the last of which has undergone a special process of purification.

About 10,000 casks of oil are annually produced by the Greenland Company, of which about one-fifth is light brown oil. The industry is a State monopoly, and no foreign vessels are allowed to sail in Greenland waters.[1]

Composition.—*Ljubarsky*,[2] by treatment of the lead salts of the fatty acids with ether, obtained 17 per cent. of a saturated acid judged to be palmitic acid, and 83 per cent. of liquid acids, which were found by Hazura's method to consist of oleic acid and physetoleic acid, the latter being the more abundant constituent.

Linolic acid was detected in Caspian seal fat by *Kurbatoff;* and *Bull* separated 11·96 per cent. of highly unsaturated fatty acids (iodine value, 330).

Fahrion[3] separated 0·79 per cent. of unsaponifiable matter, and found that 0·79 per cent. of the fatty acids was insoluble in petroleum spirit (*i.e.*, "oxidised acids"). The amount of unsaponifiable matter found by *Thomson* and *Ballantyne* in oil of different origin ranged from 0·38 to 0·51, whilst *Bull* separated 0·83 per cent.

Seal oil does not contain much free fatty acid, when in a fresh condition. Thus, *Thomson* and *Ballantyne*[4] found the percentage calculated as oleic acid to be 1·46, and 1·48 in two samples of pale oil. In the darker qualities of oil, however, the amount is much higher—*e.g.*, 8·29 per cent. (*Thomson* and *Ballantyne*); 19·95 per cent. (*Chapman* and *Rolfe*[5]).

Detection of Adulteration.—For the detection of seal oil in cod-liver oil, *Dowzard*[6] recommends the use of the oleo-refractometer. On shaking pale seal oil with alcohol at 30° C., separating it from the solvent, and drying it at 110° C., he obtained readings of + 32 to

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[1] *Board of Trade J.*, January 3, 1901.

[2] *J. prakt. Chem.*, 1898, lvii., 19.

[3] *Chem. Zeit.*, 1899, xxiii., 161.

[4] *J. Soc. Chem. Ind.*, 1891, x., 236.

[5] *Chemical News*, 1894, lxx., 1.

[6] *Analyst*, 1898, xxiii., 317.

+ 32·5 at 22° C. Cod-liver oil, on the other hand, gave much higher readings after purification in the same way (+ 44 to + 45). *Permain* obtained similar results with samples of seal oil (+ 30 and + 36).

The presence of rosin oil in seal oil can be detected by a determination of the amount of unsaponifiable matter.

SHARK OIL.

Recorded Values.

Shark Oil.

Specific Gravity at 15° C.	Acid Value.	Saponification Value.	Hehner Value.	Iodine Value.	Melting Point. °C.	Refractive Index.	Authority.
0·9177	0·88	163·5	...	136·0	...	...	Bull (*a*).
0·9163	...	161·0	86·9	114·6	...	...	Lewkowitsch (*b*).
0·9158	7·05	157·2	...	90·0	...	...	Eitner.
...	8·2	...	97·26	138·6	...	...	Fahrion.
0·9189	11·3	...	...	133·1	−4	...	Mitchell.
0·917	...	...	...	...	...	1·4783	Procter.

(*a*) Japanese. (*b*) Arctic.

Fatty Acids.

Melting Point. °C.	Solidification Point. °C.	Iodine Value.	Authority.
21·8	17·4	124·3	Mitchell.

Shark oil is obtained from the livers of different species of shark, but is probably chiefly used in admixture with other liver oils.

It contains a large proportion of unsaponifiable matter (including spermaceti). Thus *Fahrion* obtained from 0·93 to 5·27 per cent. from different kinds of oil, whilst *Allen* found from 0·7 to 17·3 per cent.

It varies in colour from light yellow to orange, or yellowish-red.

Hehner and *Mitchell* obtained 22 per cent. of an insoluble bromide from one specimen of the oil, pointing to the presence of a mixed glyceride (*cf. Cod-liver oil*, p. 587).

The presence of saturated and unsaturated hydrocarbons in the liver oils of certain species of sharks causes the analytical values of these oils to differ widely from those in the table above.

The liver oils of 12 species of Japanese sharks examined by *Tsujimoto*[1] had iodine values ranging from 91·3 to 236·6. The liver oil from the shark, Imori-zame (*Pristiurus pilosus*), was characterised by its very high iodine value. It had the following characters :—Sp. gr. at 15°/4° C., 0·8664 ; acid value, 0·32 ; saponification value, 28·2 ; iodine value (Wijs), 309·0 ; refractive index (20° C.), 1·4912 ; unsaponifiable matter, 85·5 per cent. ; insoluble bromides of fatty acids, 7·0 per cent. ; and squalene, about 79 per cent.

The oils of low specific gravity (below 0·9 at 15°/4° C.) invariably contained squalene (see p. 20).

Squalene was not present in the liver oils of five species of Japanese rays, but was a constituent of the egg oils of two species of sharks.

Three specimens of liver oil from the basking shark (*Cetorhinus maximus*), the largest of the shark tribe, contained 41·92 to 55·51 per cent. of unsaponifiable matter, in which the unsaturated hydrocarbon squalene was identified. One sample also contained about 10 per cent. of a liquid saturated hydrocarbon, $C_{18}H_{38}$.

This sample had the following characters :—Sp. gr. at 15°/4° C., 0·8839 ; acid value, 1·09 ; saponification value, 102·45 ; iodine value 178·3 ; refractive index at 20° C., 1·4773 ; and unsaponifiable matter, 41·92.

The unsaturated hydrocarbon squalene forms hexahydrohalides of the general formula, $C_{30}H_{50}6HX$, which may be crystallised, and serve for the identification of the hydrocarbon.[2]

OTHER FISH OILS.

The oils obtained from various other kinds of fish have been prepared, but, in general, little is known as to their composition, except that they contain glycerides of highly unsaturated fatty acids (*Bull*, p. 159).

The following table gives some of the values that have been recorded for such oils :—

Oil.	Specific Gravity at 15° C.	Acid Value.	Saponification Value.	Iodine Value.	Insoluble Fatty Acids.	Unsaponifiable Matter.	Authority.
					Per cent.	Per cent.	
Haddock-liver,	0·9298	...	188·8	154·2	93·3	1·1	Lewkowitsch.[3]
Herring, .	0·9215	1·8	170·9	131·0	...	10·68	Bull.[4]
,, (brown) (England),	0·9391	40·2	184·8	132·7	...	2·64	,,
Skate-liver,	0·9307	...	185·4	157·3	94·7	0·97	Lewkowitsch.
Sturgeon,	0·9236	0·23	186·3	125·3	...	24·12	Bull.
Sunfish,	0·9010	2·15	147·6	102·7	..	2·01	,,

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[1] *J. Chem. Ind., Tokyo*, 1918, xxi., 1015.

[2] *J. Ind. Eng. Chem.*, 1917, ix., 1098.

[3] *Oils, Fats, and Waxes*, 1895, 401.

[4] *Chem. Zeit.*, 1899, xxiii., 1043.

WHALE OIL.

Recored Values.

Whale Oil.

Origin.	Specific Gravity at 15·5° C.	Saponification Value.	Iodine Value.	Hehner Value.	Reichert Value	Unsaponifiable Matter.	Authority.
						Per cent.	
...	0·9193 at 15° C.	188·8	110·1	...	...	1·22	Thomson & Ballantyne.
...	...	184 4-185·5	105·8-116·2	95·2-96·7	...	0·65-1·37	Fahrion.
...	0·9225	194·2	127·7	...	...	...	Schweitzer & Lungwitz.
...	0·9223	187·9	126·4	...	...	...	,, ,,
...	0·9225	193·6	122·7	...	...	...	,, ,,
...	0·9221	191·1	121·3	...	...	...	,, ,,
...	...	188·5	...	93·5	0·7 2·0	0·9-3 72	Lewkowitsch.
Arctic refined	0·9234	185·0	117·4	...	...	2·11	Bull.
Arctic crude	0·9222	183·9	127·4	...	...	1·37	,,

Fatty Acids.

Specific Gravity at $\frac{100^\circ \text{C.}}{100^\circ \text{C.}}$	Melting Point.	Saponification Point.	Iodine Value.	Authority.
	°C.	°C.		
0·8922	...	...	...	Archbutt.
...	16	...	132·0	Schweitzer & Lungwitz.
...	14-15	...	131·0	,, ,,
...	16·2	...	130·8	,, ,,
...	18·0	...	130·3	,, ,,
...	...	Dalican's Test. 22·9-23·9	...	Lewkowitsch.

Whale oil is obtained from different species of whales (see Chap. XIII.), the blubber being rendered by the methods described in Chap. X.

Like other marine animal oils, whale oil contains highly unsaturated acids. Thus *Bull*,[1] by treatment of the sodium salts with ether, separated about 8 per cent. of fatty acids with iodine values of 201 and 206.

The nature of several of the other constituents of whale oil has not yet been determined, although palmitic acid has been identified.

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[1] *J. Soc. Chem. Ind.*, 1895, xiv., 130.

On standing in a cool place, whale oil yields a solid deposit which contains palmitin.

Schweitzer and *Lungwitz*[1] state that whale oil is in common use in the United States for lubricating and burning purposes. They consider that the only likely adulterants are mineral oil, rosin oil, cottonseed oil, maize oil, and fish oils.

In their opinion, refined whale oil should have the following characteristics :—It should be clear and pale yellow in colour, with a specific gravity of 0·921 to 0·923, an iodine value of 120 to 130, and saponification value of 190 to 200. The fatty acids should melt at or below 20° C., and should not give any reduction in Milliau's silver nitrate test.

For the characteristics of hydrogenated whale oil, see p. 455.

CLASS VIII.—VEGETABLE BUTTERS AND FATS.

Akee Oil.[1]

This fat is derived from the pulp surrounding the seeds of the akee tree, which is cultivated in Guinea and Jamaica.

It is a yellow, butter-like mass, with a peculiar odour and unpleasant taste.

The following constants were obtained by *Garsed*[2] :—

Akee Oil.

Specific gravity at 99° to 100° C. (water at 15·5° C. = 1),	0·857
Melting point,	25°-35° C.
Solidification point,	20° C.
Hehner value,	93
Saponification value,	194·6
Reichert value,	0·9
Iodine value (Hübl),	49·1
Acid value,	20·1

Fatty Acids.

Specific gravity at 99° to 100° C.,	0·8365
Melting point,	42-46
Solidification point,	38-40
Saponification value,	207·7
Iodine value,	48·4

The fatty acids distil without decomposition at 220° to 225° C.

The oil-cake from the pressed seed contains 25 per cent. of oil that can be extracted with solvents.

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[1] Holmes, *Pharmaceut. J.*, 1900, lxv., 691.

[2] *Ibid.*

BASSIA TALLOW. MOHWAH BUTTER.

Recorded Values.

Bassia Tallow.

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Reichert Value.	Hehner Value.	Refractive Index at 40° C.	Melting Point.	Solidification Point.	Authority.
						° C.	° C.	
0·8970 at 100° C.	190·8	42·1	0·44	94·86	48·2 = 1·4570	..	..	Crossley and Le Sueur (*c*).
0·9175	192·3	..	..	..	..	25·3	17·5-18·5	Valenta.[1]
..	188·4	60·4	..	..	..	42	36	De Negri and Fabris (*a*).
..	199·9	..	..	..	..	28-31	19-22	„ (*b*).
..	192·4	62	..	..	..	..	..	Lewkowitsch(*d*).
0·8943 to 0·8981 at 100° C./100° C.	187·4 to 194·0	53·43 to 67·85	0·44 to 0·88	94·69 to 94·95	1·4605 to 1·4609	23 to 29	..	Crossley and Le Sueur (*b*). (9 samples.)
0·8595 at 99°/15° C.	192·2	59·4	..	..	47·7 (Zeiss)	..	..	Revis and Bolton (*b*).
0·8624	189·8	62·4	..	..	49·3 (Zeiss)	..	..	Revis and Bolton (*a*).
..	188·2	42·6	1·31	..	47·8 (Zeiss)	..	..	Revis and Bolton (*c*).
..	179·64	47·72	3·08	95·65	57·6 (Zeiss)	..	..	Sprinkmeyer & Diedrichs (*e*).
..	170·32	50·65	..	96·15	59·6 (Zeiss)	..	..	Sprinkmeyer & Diedrichs (*f*).
..	177·88	47·73	..	95·98	59·3 (Zeiss)	..	..	Sprinkmeyer & Diedrichs (*g*).

(*a*) From *Bassia longifolia*.
(*b*) From *Bassia latifolia*.
(*c*) *Bassia butyracea*.
(*d*) Commercial.
(*e*) *B. butyracea* (crude extracted).
(*f*) *B. butyracea* (hot-pressed crude).
(*g*) *B. butyracea* (hot-pressed refined).

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
°C.	°C.		
39·5	38	..	Valenta.
45	40	..	De Negri and Fabris.
39·7-40·3	..	56·6	Lewkowitsch.
58·4	..	..	Sprinkmeyer and Diedrichs.

According to *Crossley* and *Le Sueur*,[2] the fat obtained from the seeds of *Bassia longifolia* is known as *Mohwah butter* or *Mowrah seed*

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[1] *Dingler's polyt. J.*, ccli., 461.

[2] *J. Soc. Chem. Ind.*, 1898, xvii., 991.

oil, whilst that from *Bassia latifolia* is termed Mahua butter or Illipé butter, but in commerce the seeds are frequently mixed and the fats sold under either name.

Lewkowitsch states that the commercial article is a mixture of these two fats.

B. latifolia grows in Central India, whilst *B. longifolia* is found in Southern India. The seeds of the latter are rounder than those of the other two species, whilst those of *B. butyracea*, which is also an Indian product, are the smallest. The fat is locally known as " Phulwa " or " Phulwara " butter.

The freshly-expressed fat is pale yellow, and has an aromatic odour and taste. When exposed to the air it is bleached and becomes rancid.

A specimen of fat that had thus been exposed was found by the present writer to have an iodine value of 22·9.

This fat is largely employed in the manufacture of soap and candles, and in India is used as an edible fat.

The fat from the seeds of *Bassia Mottleyana* is used by the Dyaks as a food, but is not yet a commercial product. It was found by *Brooks*[1] to have analytical characteristics very similar to those of the fats from the other species.

BORNEO TALLOW.[2]

Recorded Values.

Borneo Tallow.

Free acid as stearic acid, per cent.,	9·5-10
Hehner value,	95·68
Reichert-Meissl value,	0·3-0·5
Melting point, commences	35°-36° C.
,, ends,	45° C.

Fatty Acids.

Melting point,	53·5°-54° C.
Molecular equivalent,	283·7
Iodine value,	29·9-30·9

Borneo tallow is derived from the seeds of a variety of plants belonging to the *Dipterocarpeæ*, of which the best known is *Shorea stenoptera*, which grows in North-West Borneo.

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[1] *Analyst*, 1909, xxxiv., 207.

[2] Geitel, *J. prakt. Chem.*, 1887, xxxvi., 515.

The seeds are imported into this country under the name of "Pontianak illipé nuts," and the fat is obtained from these by expression.

When freshly expressed it is pale green in colour, but on exposure to the air changes to yellow and finally to white. When broken, the fractured surfaces exhibit a crystalline granular structure.

It has an odour and taste recalling those of cacao butter, and is used as a substitute for that fat under the name of "Green butter."

According to *Geitel*, it consists of glycerides of stearic and oleic acids, the former being in the proportion of 66 per cent.

It is a suitable material for the manufacture of soap and candles.

Bolton and *Revis*[1] use the following modification of Halphen's test to distinguish this fat from cacao butter:—One gramme of the filtered fat is dissolved in 2 c.c. of a mixture in equal parts of carbon tetrachloride and petroleum spirit, and 2 c.c. of the mixture are cooled in a test-tube immersed in water. A solution of bromine in an equal volume of carbon tetrachloride is added, drop by drop, with constant shaking, until the colour of the bromine persists. The tube is then closed and allowed to stand, and if, after fifteen minutes, the solution remains clear, not more than 10 per cent. of cacao butter, if any, can be present. A turbidity indicates the probable presence of cacao butter. A similar turbidity is given, however, by fat from the seeds of a species of *Gutta*, but is flocculent in form, whereas the cacao butter turbidity is not flocculent.

BUCHANANIA LATIFOLIA FAT.[2]

Recorded Values.

Buchanania Latifolia Fat.

Specific Gravity at $\frac{100° C.}{100° C.}$	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Viscosity compared with Water at 140°F.	Refraction at 40° C.		Melting Point.	Authority.
							Scale Divisions.	Refractive Index.		
									°C.	
0·8941	15·03	195 4	54·73	0·33	95·80	3·90	48·8	1·4584	32·0	Crossley & Le Sueur.
0·8943	40·11	191·8	59·92	...	94·87	3·69	...	...	32·0	,,

This fat is contained in the seeds of *Buchanania latifolia* to the extent of 30 to 40 per cent., but, according to *Crossley* and *Le Sueur*, is seldom expressed, owing to the natives using the seeds as a sweetmeat.

The fat is orange in colour, and closely resembles the fat of *Bassia latifolia* (Mahua butter) in its chemical and physical characteristics.

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[1] *Analyst*, 1913, xxxviii., 201.

[2] Crossley and Le Sueur, *J. Soc. Chem. Ind.*, 1898, xvii., 992.

CACAO BUTTER.

Recorded Values.

Cacao Butter.

Origin.	Specific Gravity.	Acid Value.	Saponification Value.	Reichert-Meissl Value.	Iodine Value.	Refractive Index.	Melting Point.	Solidification Point	Authority.
							° C.	° C.	
Commercial samples,	...	1·82-4·49	191·8-194·5	0·38-0·94	34·27-36·99	...	26·6-28	...	Lewkowitsch.
Extracted in laboratory,	...	1·95	192·9	0·50	35·65	...	28·4	...	,,
Sample kept 10 years in sealed bottle,	...	4·60	192·0	0·20	36·92	...	27·0	...	,,
English, fresh,	...	1·65	193·5	0·38	35·37	...	28-23	...	,,
,, ,,	...	1·39	193·1	0·33	34·86	...	28	...	,,
Dutch, ,,	...	1·11	192·8	0·83	34·55	...	27·2-33	...	,,
...	0·8577 at $\frac{98^\circ\text{ C.}}{15{\cdot}5^\circ\text{ C.}}$	...	...	...	...	...	...	...	Allen.
...	...	...	195	...	33·4-37·5	...	32·0-33·6	...	Filsinger.
...	...	...	...	...	32·8-41·7	40° C. 1·4565-1·4578	...	...	Strohl.
...	...	...	193·6	...	36·6	...	28-30	21·5-23	De Negri & Fabris.
...	0·887 at 60° C.	...	...	...	...	1·450 at 60° C.	...	...	Procter.
Commercial,	0·964-0·974 at 15° C.	1·0-2·3	...	...	32-37·7	...	30-34	...	Dieterich.
...	0·892 at 50° C.	0·5	194·4	...	34·4	...	34·5	...	Klimont.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
° C.	° C.		
48-53	45-47	39·0	De Negri and Fabris.
...	Dalican's Test. 47·2-49·2	...	Lewkowitsch.

Source.—Cacao butter is contained in the seeds of the cacao tree (*Theobroma cacao*), from which it is expressed in large quantities in the manufacture of chocolate. According to *Rieck* (Eng. Pat. 19,160, 1898) a much larger proportion of fat is expressed by grinding the roasted and hulled beans into coarse particles instead of into fine powder, owing to its being possible to apply greater pressure in the former case. The residue is stated to contain only about 10 per cent. of fat as against 30 to 35 per cent. left by the usual process.

Composition.—The following fatty acids have been stated to be present as glycerides in cacao butter:—Stearic, palmitic, lauric, oleic, linolic, arachidic, and theobromic acids.

The occurrence of theobromic acid, $C_{64}H_{128}O_2$ (*Kingzett*), has been disputed by *Graf*.

Hehner and *Mitchell* found the mixed fatty acids to contain about 40 per cent. of stearic acid. According to *Farnsteiner*,[1] the fatty acids contain 59·7 per cent. of saturated acids, and 31·2 per cent. of oleic acid.

Mixed Glycerides.—*Klimont*,[2] by fractional crystallisation of the fat from acetone, has isolated the following substances, two of which he regards as mixed glycerides:—

i. A fraction melting at 70° C., and having an iodine value of 0. This was regarded as a mixture of tripalmitin and tristearin.

ii. A fraction (m.p. 31° to 32° C.), with saponification value, 196·4; iodine value, 28·9; and empirical formula $C_{55}H_{104}O_6$. This was judged to be a mixed triglyceride, oleo-palmito-stearin.

iii. A fraction melting at 26° to 27° C., and having iodine value, 31·7; saponification value, 210; and empirical formula $C_{51}H_{96}O_6$. This was also considered to be a mixed glyceride containing the radicles of myristic, palmitic, and oleic acids, and possibly of some still lower acids. Triolein was not detected in the fat.

Elementary Composition.—According to *Schädler*, cacao butter has the following elementary composition:—Carbon, 75·20; hydrogen, 11·90; and oxygen, 12·90 per cent.

Properties and Tests of Purity.—Cacao butter is very pale yellow in colour, and has the odour of chocolate. It is comparatively hard, and can be broken between the fingers, the fractured surfaces showing indications of crystalline structure.

Acid Value.—In the freshly-expressed condition cacao butter does not contain much free fatty acid, but, on standing, the proportion gradually increases (see *Table of Values*).

It has been stated that cacao butter does not turn rancid. It has been shown, however, by *Dieterich*, and subsequently by *Lewkowitsch*,[3] that rancidity does take place, though not rapidly.

A high acid value points to the presence of added stearic acid.

Iodine Value.—This varies within comparatively narrow limits, whatever the origin of the fat may be.

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[1] *Zeit. Untersuch. Nahr. Genussm.*, 1899, ii., 1.

[2] *Ber. d. d. chem. Ges.*, 1901, xxxiv., 2636; *Monatsh. f. Chem.*, 1902, xxiii., 51.

[3] *J. Soc. Chem. Ind.*, 1898, xviii., 556.

Strohl has observed a parallelism between the iodine value and the refractive index.

A high iodine value points to the presence of vegetable oils, whilst a low one may be due to the addition of coconut oil.

Acetyl Value.—This was found to be 1·97 in the case of one sample of the fat examined by *Lewkowitsch.*

Solubility in Different Solvents—Alcohol.—Cacao butter is insoluble in alcohol of 90 per cent. strength, but dissolves in five times its weight of boiling absolute alcohol.

Crismer found the critical temperature of solution to be 126° C.

Ether.—The German Pharmacopœia requires that cacao butter, on treatment with twice its quantity of ether, shall give a solution which remains clear for 24 hours at 12° to 15° C. (*vide infra*).

Valenta Test.—*Valenta* found that a solution of cacao butter, in boiling glacial acetic acid, became turbid at 105° C.

Hager's Aniline Test.—One gramme of cacao butter is dissolved in 2 to 8 grammes of aniline, and the solution allowed to stand for an hour at 15° C. In the case of pure cacao butter, an oily layer is formed above the aniline, and does not crystallise for several hours. When tallow, stearic acid, or paraffin wax in small quantity is present, solid particles can be observed suspended in the oily layer; whilst beeswax or large quantities of paraffin wax cause the fatty layer to solidify. When much stearic acid is present, the entire contents of the tube solidify.

Detection of Adulteration.—Cacao butter is liable to be adulterated with stearic acid, tallow, vegetable oils, coconut oil, paraffin wax, and beeswax.

Stearic Acid is indicated by a high acid value, and by shaking the sample with an aqueous solution of sodium hydroxide, and acidifying the liquid. It can also be detected by Hager's aniline test.

Tallow.—This is detected by the aniline test, and by the behaviour of the sample towards ether, in the following test:—

Björklund's Ether Test.—Three grammes of the fat are shaken in a stoppered tube with about 6 grammes of ether at 18° C. In the presence of wax a clear solution will not be obtained, even on heating. Should, however, the fat dissolve completely, the tube is immersed in water at 0° C., and a note taken of the time required for the liquid to become turbid, and to become clear again after removal of the tube from the water.

In this way the following results were obtained:—

	Turbidity at 0° C. after Minutes.	Clear Solution again after Minutes.
Pure Cacao Butter, . . .	10-15	19-20
Cacao butter + 5 per cent. tallow,	8	22
„ + 10 „ . „	7	25

Filsinger[1] describes a modification of this test :—Two grammes of the fat are melted in a graduated tube and shaken with 60 c.c. of a mixture of four parts of ether (sp. gr. 0·725) and 1 part of alcohol (sp. gr. 0·810) ; when pure, cacao butter should give a clear solution which does not become turbid on cooling to 0° C.

Lewkowitsch (*loc. cit.*) points out that the manner in which the crystallisation of the fat from ether occurs is a good test. Cacao butter separates in tufts at the bottom and sides of the tube, whilst in the presence of 5 per cent. of tallow the crystals separate in flakes.

Phytosterol Test.—The unsaponifiable matter should only show the crystalline form of phytosterol. In the case of artificial mixtures, *Lewkowitsch* did not obtain the mixed form of crystals, each variety crystallising separately.

Coconut Oil.—This will be indicated by the lower iodine value and melting point of the fatty acids, and by the increased saponification and Reichert values, and by the Polenske test.

According to *Hager*, its solubility in alcohol (90 per cent.) is 10 times as great as that of cacao butter.

Extended Reichert Value.—*Wauters*[2] recommends his process (*cf.* Chap. VIII.) for the detection of coconut oil in cacao-butter, the difference between the two fats being shown by the following examples :—

Fat.	Soluble Volatile Acids.			Insoluble Volatile Acids.		
	1st Distillation.	2nd Distillation.	Total.	1st Distillation.	2nd Distillation.	Total.
Cacao butter,	0·10	0	0·10	0·25	0·15	0·4
Coconut oil,	7·10	4·30	11·40	7·85	7·55	15·4

Paraffin Wax.—This lowers the saponification value and increases the amount of unsaponifiable matter.

De Negri and *Fabris*[3] describe the following method for its quantitative determination :—The fat is saponified and the soap solution heated with acetic anhydride, with the result that the paraffin wax remains undissolved, and, rising to the surface, can be collected and weighed. See also *Hager's Aniline Test* (*supra*).

Beeswax.—This is indicated by the decrease in the saponification and iodine values, and by the increase in the proportion of unsaponifiable matter.

Vegetable Oils raise the iodine value and lower the melting point of the fat and fatty acids.

[1] *Zeit. anal. Chem.*, 1880, xix., 247.
[2] *Bull. de l'Ass. belge Chim.*, 1901, xv., 131.
[3] *Zeit. anal. Chem.*, 1894, xxiii., 569.

CHINESE VEGETABLE TALLOW (STILLINGIA TALLOW).

Recorded Values.

Chinese Tallow.

Specific Gravity at 15° C.	Acid Value.	Saponification Value.	Reichert Value.	Iodine Value.	Melting Point.	Solidification Point.	Authority.
					° C.	° C.	
0·918	..	..	..	..	44·5	..	Thomson and Wood.
..	..	200·3	..	32·1-32·3	43-46	24·2-26·2	Lewkowitsch (*a*).
..	..	185·6	0·2	22·87	35·8	..	Mitchell (*a*).
..	2·2	179	..	45·2	44	34	De Negri and Fabris (*a*).
..	..	178·7-179	..	52·5-53	37-38	27-29	„ (*b*).
..	..	203·3	..	28·5	39-42	32	Hobein (*b*).
0·9182 to 0·9217	..	198·5 to 202·2	..	28·5-37·7	36·5-44·1	27·2-31·1	De Negri and Sburlati.
..	..	206·64	0·88	29·78	..	..	Sprinkmeyer and Diedrichs.

Fatty Acids.

Melting Point.	Solidification Point.	Saponification Value.	Iodine Value.	Authority.
° C.	° C.			
..	52·1-52·5 (Dalican.)	..	34·2-34·3	Lewkowitsch (*a*).
53·5	..	..	..	Mitchell (*a*).
47	42	182·1	47	De Negri and Fabris (*a*).
39-40	34-35	181·2-182	54·1-54·8	„ „ (*b*).
49	48	206·4	29·6	Hobein (*b*).
53·0-56·9	45·2-47·9	..	30·3-39·5	De Negri and Sburlati.
54·3	..	..	..	Sprinkmetyer and Diedrichs.

(*a*) Commercial samples. (*b*) Extracted from seeds.

The commercial fat known as vegetable tallow is obtained from the seeds of numerous varieties of plants, such as *Croton sebiferum*, *Stillingia sebifera*, etc.; this fact accounts for the great variations in the recorded values.

According to *De Negri* and *Sburlati*,[1] the Chinese obtain it by steaming the husked seeds until soft, beating them with wooden hammers, and placing the crushed mass in hot sieves, through which the melted tallow falls into pots.

The seeds of *Stillingia sebifera* contain about 40 per cent. of fat, of which 22 per cent. is solid fat surrounding the kernel, and the remainder oil within the kernel.

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[1] *Chem. Zeit.*, 1897, xxi., 5.

Sprinkmeyer and *Diedrichs*[1] separated from the kernels 62 per cent. of a light yellow oil, which had an iodine value of 154·9 and yielded 20 per cent. of insoluble bromide melting at 147° C.

According to *Maskelyne*, the solid fat consists of palmitin and olein. The absence of stearin is confirmed by the experiments of *Hehner* and *Mitchell*,[2] but, seeing that the oil extracted from the kernels has a high iodine value and possesses drying properties (see *Stillingia oil*), it is improbable that oleic acid is the only unsaturated fatty acid present.

A specimen of this fat examined by the present writer contained 10·1 per cent. of glycerol.

The acid value of the fats examined by *De Negri* and *Fabris* was 2·4, whilst *Lewkowitsch* obtained values of 7·07 to 7·51 with different commercial samples.

Vegetable tallow is exported in large quantities to Europe, where it is used in the manufacture of soap and candles.

COCONUT OIL.

Recorded Values.

Coconut Oil.

Specific Gravity.	Hehner Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index.	Melting Point.	Solidification Point.	Authority.
° C.					At 60° C.	° C.	° C.	
...	...	253·4 to 262	8-9	...	...	23-28	14-20	De Negri & Fabris.[3]
0·9115 at 40°	...	...	...	...	...	20-28	16-20·5	Allen.
0·8736 ,, 99° (water at 15·5° = 1)	...	255-260	9-9·5	7·5	1·441	23-24	22-23	Thoerner.
...	88·6-90·5	...	...	...	...	...	...	Lewkowitsch.
0·897 at 60°	...	...	...	...	1·442	...	...	Procter.
0·9030 ,, 100°	(*a*) ...	258·2	8·54	6·71	...	23·5	...	Crossley and Le Sueur.
0·9040 ,, 100°	(*b*) 82·35	255·6	8·41	6·79	...	24·5	...	,,
0·9042 ,, 100° (water at 100° = 1)	(*c*) ...	255·5	8·25	6·65	...	25	...	,,
0·9228 at 24°	(*d*) ...	257·4	7·71	...	...	...	...	Lane.
0·9223 ,, 24°	(*e*) ...	...	6·17 6·27	...	At 20° C. 1·4550 1·4553	...	...	Merrill

(*a*) Malabar oil. (*b*) Bengal oil. (*c*) Bombay oil.
(*d*) Oil extracted with ether. (*e*) Expressed oil.

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[1] *Zeit. Untersuch. Nahr. Genussm.*, 1914, xxvii., 132.

[2] *Analyst*, 1896, xxi., 328.

[3] *Zeit. anal. Chem.*, 1894, xxxiii., 571.

Fatty Acids.

Specific Gravity at 99° C.	Melting Point.	Solidification Point.	Saponification Value.	Mean Molecular Equivalent.	Iodine Value.	Refractive Index at 60° C.	Authority.
	° C.	° C.					
...	25-27	16-18	...	...	8·6-8·9	...	De Negri and Fabris.
0·8354	...	...	...	...	...	...	Allen.
...	24-25	20	258	...	8 5-9	1·4295	Thoerner.
...	...	...	...	196-204	...	...	Alder Wright.
		Dalican's Test.			Liquid Acids.		
..	...	21·2-25·2	...	211 (*a*)	...	...	Lewkowitsch.
...	...	...	...	...	54	...	Wallenstein and Fink.
...	...	23	...	...	18·58	...	Lane.

(*a*) Ceylon oil.

Source.—This fat is obtained from the kernels of the nuts of the cocoa palm (*Cocos nucifera, C. butyracea*), which grows in all tropical countries within about 23 degrees of the Equator, and is specially cultivated in Ceylon and on the Malabar coast (Cochin), where most of the exported oil is expressed. Of late years large quantities of the dried kernels (copra) have also been exported, and the oil expressed in Europe (*Schädler*). The methods of obtaining the oil are described in Chap. IX.

Experiments made in the Philippines have shown that the Californian method of treating fruits with the fumes of burning sulphur is applicable to the coconut. The nuts are opened and treated with burning sulphur in a closed vessel, and may then be kept for two weeks without moulds developing.[1] In the Manila markets the best grade of coconut oil known as "Cebu sundried" fetches about 2s. 6d. per 100 kilos. more than the poorest quality known as "Laguna."

From an investigation of *Brill*, *Parker*, and *Yates*[2] into the cause of the poor quality of Philippine copra, it was found that the oil from it was discoloured and rancid, and contained from 5 to 20 per cent. of free fatty acids. In the case of copra containing from 10 to 20 per cent. of moisture moulds rapidly develop and cause a loss of 25 per cent. or more of the total oil present. To obviate this rapid drying is necessary, and it has been found that copra can be dried in a current of air at 70° to 100° C. without loss of oil. Good copra should contain from 4 to 6 per cent. of moisture and 65 per cent. of oil (calculated on the dry material) with an acidity of less than 1 per cent. as oleic acid, and should be free from dirt and smoke.

It has been shown by *Parker* and *Brill*[3] that the oil cannot be readily expressed from freshly-grated coconut, over 60 per cent. of the total oil remaining in the cake after expression at 1,000 lbs. per square

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[1] Cox, *Philippine J. Sci.*, 1917, A. xii., 49.

[2] *Ibid.*, 55.

[3] *Philippine J. Sci.*, 1917, A, xii., 87.

inch. By treating the material with water and live steam for three hours before expression 80 per cent. of the total oil is removed by a single expression. The best method of separating the oil from the residual emulsion was found to be by chilling it for 24 hours at 15° C., to separate the aqueous layer, to melt the solid fat at a low temperature, and to pass it through a filter press. Oil thus prepared has a pleasant odour, and is free from acidity and rancidity.

A high degree of rancidity is usually indicated by a high oxidisability value (p. 185).

Composition.—Coconut oil consists principally of trilaurin, trimyristin, and triolein, with smaller quantities of palmitin, caprin, caproin, caprylin, and the glycerides of other volatile fatty acids.

Ulzer [1] found commercial purified samples to contain about 2·33 per cent. of glycerides of volatile fatty acids (chiefly caproic and caprylic acids), and about 10·45 per cent. of olein, which was identified and approximately estimated by conversion into dihydroxystearic acid. The remainder consisted of the glycerides of lauric, myristic, and capric acids. The presence of palmitin was considered doubtful.

By the method of alcoholysis, however (p. 143), *Elsdon* [2] found a specimen of coconut oil to consist of glycerides of the following acids in approximately the proportions given:—Caproic, 2; caprylic, 9; capric, 10; lauric, 45; myristic, 20; palmitic, 7; stearic, 5; and oleic acid, 2 per cent.

Hehner and *Mitchell* have shown that in their method of determining stearic acid, coconut oil fatty acids yield no deposit.

Properties—*Melting Point.*—This varies considerably with the age and the manner in which the oil was obtained. Thus, according to *Schädler*, the ordinary commercial Ceylon or Cochin oil melts at 24° to 24·5° C., whilst the freshly-expressed oil melts at 22° to 22·5° C., and the cold-drawn oil, which is used by the natives for food, and is rarely met with in commerce, melts below 20° C., and begins to solidify at 12° to 13° C. Brazilian coconut oil has a considerably higher melting point (26° to 27° C.).

Specific Gravity.—The specific gravity of commercial coconut oil is considerably higher than that of butter; but this difference is no longer present in deodorised "vegetable butter." Thus, *Herz* [3] gives the following comparative figures:—

Specific Gravity at 35° C.

Deodorised coconut oil,	0·9124
Butter fat,	0·9121
Margarine,	0·9017

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[1] *Chem. Rev. Fett Ind.*, 1899, vi., 203.

[2] *Analyst*, 1913, xxxviii., 8.

[3] Benedikt, *Analyse der Fette*, 2nd Ed., 380.

Acidity.—Commercial Ceylon oil contains about 5 to 10 per cent. of free fatty acids, whilst the copra oil contains a far larger proportion. In one sample *Lewkowitsch*[1] found as much as 25 per cent. calculated as oleic acid; whilst *Crossley* and *Le Sueur*[2] found 2·5 and 2·98 per cent. in Indian oils, and 8·86 per cent. in a specimen of Malabar oil.

Coconut oil readily becomes rancid, and develops an unpleasant odour and taste.

Solubility in Alcohol.—Coconut oil resembles cacao butter in being fairly soluble in alcohol, one part being dissolved by two parts of 90 per cent. alcohol at 60° C.

Vandam utilises the difference in the solubility of the different fatty acids in alcohol as a means of detecting coconut oil in butter and other animal fats (*vide infra*).

Reichert Value.—A characteristic feature of coconut oil is the large proportion of volatile acids that it contains. Owing to this, it has a high Reichert value, and is sometimes used to make butter containing foreign fats appear normal in this respect.

In order to detect coconut oil in butter, *Wauters* recommended an extension of the Reichert process (*vide infra*).

Saponification Value.—The presence of so large a proportion of the glycerides of lauric and myristic acids causes coconut oil to have a high saponification value. The fats that most closely resemble it in this particular are palm oil (about 202) and butter fat (about 227).

Coconut oil is readily saponified by strong alkalis. A large addition of salt is required to cause the soap to separate.

Heat of Combustion.—*Merrill*[3] obtained the following results in calories per gramme with samples of coconut oil :—

Oil extracted with ether, ...	9,027
Oil expressed, ...	9,066

Manufacture of "Vegetable Butter."—Various methods are in use for deodorising coconut oil and rendering it suitable as a substitute for butter (see Chap. XI.). As thus prepared, coconut oil is sold under different fancy names, such as "vegetaline," "vegetable butter," "lactine," etc.

Benedikt[4] gives the following as the characteristics of such purified coconut oil :—

Melting point, ...	26·5° C.	(*Fresenius*).
Solidification point, ...	24° to 25° C.	,,
Specific gravity at 35° C., . . .	0·9124	(*Herz*).
Oleo-refractometer reading, . .	− 59°.	
Melting point of fatty acids, . .	25·5° C.	(*Fresenius*).
Solidification point, ...	19·9° C.	,,

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[1] *Oils, Fats, and Waxes*, 2nd Ed., 538.
[2] *J. Soc. Chem. Ind.*, 1898, xvii., 993.
[3] *Maine Agric. Exper. Stat. Bull.*, 1900, [65], 111.
[4] *Analyse der Fette*, 2nd Ed., 380.

The saponification, iodine, and Reichert values are similar to those of the ordinary commercial oil.

Analyses of mixtures containing coconut oil, cotton-seed oil, beef fat, etc., have been published by *Kitto*, and by *Bodmer*.[1]

Detection of Adulteration.—Coconut oil is unlikely to be adulterated to any extent.

It is used in the manufacture of margarine, and may therefore be met with in butter. It is also used to adulterate lard and cacao butter.

Detection of Coconut Oil in Butter, etc.—*Vandam*[2] recommends the following method of detecting coconut oil in butter or other animal fats:—

I. *Determination of Fatty Acids Soluble in Alcohol.*—Five grammes of the fat are saponified with 25 c.c. of alcoholic potassium hydroxide (8 grammes in a litre of alcohol of specific gravity 0·832). An additional quantity of the same alcoholic solution is then added so as to yield alcohol of the required percentage after dilution to 100 c.c.

The diluted soap solution is cooled to 15° C., decomposed with 25 c.c. of standard sulphuric acid, cooled to 15° C., filtered, and the fatty acids in the filtrate titrated with $\frac{N}{2}$ sodium hydroxide solution. The fatty acids on the filter are dried, and their volume determined when suspended in 10 c.c. of the alcohol. A correction is also made for the volume of the precipitated sulphate. In this way *Vandam* obtained the following results, representing the proportion of fatty acids expressed in terms of semi-normal sodium hydroxide solution, soluble in the different strengths of alcohol at 15° C.

Fat.	Alcohol.					
	50 per cent.	55 per cent.	60 per cent.	65 per cent.	70 per cent.	80 per cent.
Coconut oil, .	4·3	13·3	44·2	44·0	...	...
Butter, . .	...	8·5	10·9	25·8	27·7	30·0
Margarine, .	...	...	3·6	9·5	22·8	26·2

II. *Determination of Fatty Acids Soluble in Alcohol, Insoluble in Water.*—Fifty c.c. of the solution of fatty acids in 60 per cent. alcohol obtained in the preceding test are evaporated to three-fourths of the volume, then mixed with boiling water, cooled to 15° C. and filtered. The precipitated fatty acids are washed with boiling water, cooled, filtered, dissolved in boiling alcohol, and titrated with semi-normal sodium hydroxide solution.

The following results were thus obtained by *Vandam*:—Butter (4 samples), 4·6 to 5·2; margarine, 3·1; and coconut oil, 42·0.

Extended Reichert Value.—The method of extending the Reichert-Meissl method so as to include the insoluble volatile fatty acids that distil under empirical conditions is described in Chap. VIII.

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[1] *Analyst*, 1895, xx., 32, 33.

[2] *J. Pharm. Chim.*, 1901, vi., 273.

The following results, representing c.c. of $\frac{N}{10}$ alkali, were obtained by *Wauters*:—[1]

Fat.	Soluble Volatile Acids.			Insoluble Volatile Acids.		
	1st Distillation.	2nd Distillation.	Total.	1st Distillation.	2nd Distillation.	Total.
Coconut oil, . .	7·1	4·3	11·4	7·85	7·55	15·4
Butter (3 samples), .	21·2-23·8	5·0-5·4	26·2-29	0·4-0·6	0·3-0·4	0·8-0·9
Margarine, . .	0·2	0·2	0·4	0·5	0·05	0·55
Mixture of butter and coconut oil (3 : 1),	18·4	5·8	24·2	2·8	2·2	5·0

The theoretical values for the mixture were:—Soluble volatile acids, 23·7; and insoluble volatile acids, 4·55.

Kirschner's Process.—This extension of the Reichert process distinguishes between the amounts of caprylic and butyric acids in the distillate (see p. 244).

Revis and *Bolton* [2] have shown that this method is a useful adjunct to Polenske's method (pp. 244, 659), and to that of *Shrewsbury* and *Knapp* (p. 661), which is based upon the fact that the predominating fatty acid in coconut oil is lauric acid.

Another method has been based by *Revis* and *Bolton* [3] upon the degree of solubility in alcohol of the barium salts of the insoluble fatty acids (see *Butter*, p. 661).

COTTON-SEED STEARINE.

Recorded Values.

Cotton-Seed Stearine.

Specific Gravity.	Melting Point.	Hehner Value.	Saponification Value.	Iodine Value	Maumené Test.	Solidification Point.	Authority.
	° C.				° C.	° C.	
0·867 at 100° C.	30-31	96·3	194·6	93·6	48	...	Hart.[4]
0·8684 at $\frac{99^\circ\text{C.}}{15{\cdot}5^\circ\text{C.}}$	40	...	...	88·7	...	31-32·5	Allen.
...	26-29	...	...	...	...	...	De Negri & Fabris.
0·9115 at 37·7°C.	32·2	...	...	...	...	...	Muter.
...	32-39	...	...	...	...	...	Mayer.
...	...	...	194·8-195·1	92·7-92·8	...	...	Lewkowitsch.

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[1] *Bull. de l'Ass. belge Chim.*, 1901, xv., 25.

[2] *Analyst*, 1911, xxxvi., 336.

[3] *Ibid.*, 1913, xxxviii., 255.

[4] *Chem. Zeit.*, 1893, xvii., 1522.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
°C.	°C.		
45·5-46·5	...	...	Hart.
27-30	...	94·3	De Negri and Fabris.
	Dalican's Test.		
...	34·9-35·1	...	Lewkowitsch.

Cotton-seed stearine is the solid fat that deposits on chilling cotton-seed oil. In America this deposit is separated and pressed, leaving what is known as " winter " cotton-seed oil.

It is a soft, yellow, butter-like mass, which gives the reactions of cotton-seed oil.

It is used in the manufacture of soap and of margarine. It consists principally of palmitin. A specimen examined by *Hehner* and *Mitchell*[1] contained only 3·3 per cent. of stearic acid. *Hart* found 0·56 per cent. of unsaponifiable matter in a sample of the fat.

Vegetal.—This is the name given to a lard substitute consisting chiefly of cotton stearine. According to *Wirthle*,[2] it is a yellow semi-solid fat, with an iodine value of 89·24, saponification value of 196·1, and refractometer reading at 25° C. of 63·3. It can be readily identified in lard by the phytosterol tests.

DIKA OIL (WILD MANGO OIL).[3]

Recorded Values.

Dika Oil.

Specific Gravity.	Free Fatty Acid.	Iodine Value.	Melting Point.	Authority.
	Per cent.		°C.	
0·820	..	30·9-31·3	29	Schädler.
..	4 to 10	30·9	30 to 32	Lemarié.

This fat is obtained from the seeds of the African mango tree, *Mangifera gabonensis*, which grows on the West Coast of Africa. The yield is about 60 to 65 per cent.

In the fresh condition it is perfectly white and has a pleasant aromatic odour and taste ; but it becomes rancid after some time, and turns yellow.

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[1] *Analyst*, 1896, xxi., 328.

[2] *Chem. Zeit.*, 1899, xxiii., 250.

[3] Schädler, *Technologie der Fette*, 779.

According to *Lemarié*,[1] it contains the glycerides of lauric, myristic, and palmitic acids.

It is readily saponified, and is used in the manufacture of candles, and as a substitute for coconut oil in marine soaps.

It closely resembles cacao butter, and cannot be distinguished from the latter by Björklund's ether test.

According to *Schädler*, it contains laurin, myristin, palmitin, and ree fatty acids.

I'SANO SEED OIL.[2]

This oil is contained, to the extent of 60 per cent., in the seeds of the I'Sano or Ungueko, a large tree belonging to the *Oleaceæ*, growing in the French Congo.

The oil is a viscous reddish-coloured liquid with a fish-like odour. It does not solidify when chilled to —15° C.

According to *Hébert*, it contains 80 per cent. of liquid fatty acids (consisting of 15 per cent. of oleic acid and 75 per cent. of linolic acid); 10 per cent. of a previously unknown white unsaturated solid acid, to which *Hébert* gave the name *Isanic acid;* and 12 to 13 per cent. of glycerol.

It is a drying oil, and, in Hébert's opinion, might be used with advantage as a substitute for linseed oil.

In the elaidin reaction it gives a viscid red mass.

The specimen examined by *Hébert* had a specific gravity of 0·973 at 23° C., and in the Maumené test showed a rise of 117° C.

JAPAN WAX.

Source.—Japan wax is obtained from the berries of various species of Rhus (*R. succedanea*, etc.), which are cultivated in Japan. The berries are kept for some time, then crushed and winnowed, and the powder pressed in wooden wedge-presses. The crude wax (about 15 per cent.) is melted and pressed through cotton-bags into cold water, after which it is exposed to the action of the sun in thin layers, until bleached.

According to *Lemarié*,[3] the last traces of wax are removed by adding about 10 per cent. of perilla oil and again pressing the mass. This accounts for the variations in the hardness of the commercial wax.

According to *Ahrens* and *Hett*,[4] accelerated methods of artificial bleaching are now in use to meet the increasing demand for the wax, and they consider that this may account for the fact that samples with low iodine values (4) are not now met with in commerce.

Composition—*Palmitic Acid.*—Japan wax is usually considered to consist essentially of glycerides of palmitic acid with free palmitic acid. *Hehner* and *Mitchell* separated a fatty acid which corresponded

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[1] *Bull. Imp. Inst.*, 1903, [4], 206.

[2] Hébert, *Bull. Soc. Chim.*, 1896, xv., 935.

[3] *Bull. Imp. Inst.*, 1903, [4], 206.

[4] *Zeit. angew. Chem.*, 1901, 684.

JAPAN WAX.

Recorded Values.

Japan Wax.

Specific Gravity.	Acid Value.	Saponification Value.	Iodine Value.	Acetyl Value.	Refractive Index.	Melting Point.	Solidification Point.	Authority.
						° C.	° C.	
0·9018 at $\frac{60°C.}{15·5°C.}$ 0·8755 at $\frac{99°C.}{15·5°C.}$	...	214-221·3	...	...	...	56	53	Allen.
0·970-0·980 at 15° C.	...	...	...	...	...	53·5-54·5	40·5-41 rising to 45·5-46	Schädler.
...	21·7-32·6 (*a*)	217·5-237·5	8·3- 8·5 (*a*)	...	...	...	...	Geitel and van der Want.
...	11·2-12 (*b*)	206·6-212	11·9-12·8 (*b*)	...	...	...	...	Ahrens and Hett.
...	...	214·9	4·9- 6·6	17·25-26·55	...	...	...	Lewkowitsch.
0·907 at 60° C.	...	...	...	...	1·450 at 60°C.	...	...	Procter.
...	...	...	...	...	Butyro-refractometer at 71°C. 47	...	...	Werder.
0·908	...	...	...	...	...	54	..	La Wall.
1·006 (crude)	...	...	...	...	...	53-54	40·5-41	Lemarié.
0·970-0·980 (bleached)	...	...	...	...	...	...	...	Lemarié.

Fatty Acids.

Specific Gravity at 99° C. (Water at 15·5° = 1).	Melting Point.	Solidification Point.	Saponification Value.	Iodine Value.	Authority.
	° C.	° C.			
0·848	56-57	53-56·5	215·2 (*c*)	...	Allen.
...	...	...	212·2-215·7	10·6	Geitel and van der Want.
...	...	Dalican's Test. 58·8-59·4	...	...	Lewkowitsch.

(*a*) Four commercial samples. (*b*) Extracted in laboratory. (*c*) Calculated from molecular equivalent.

with the characteristics of palmitic acid, having a melting point of 61·5° C., and a molecular equivalent of 255. It is a remarkable fact, however, that this palmitic acid should have prevented the crystallisation of stearic acid in their method of determining the latter acid.[1]

Japanic Acid.—*Geitel* and *van der Want*,[2] by fractionally precipitating the mixed fatty acids with magnesium acetate, obtained a crystalline dibasic acid, melting at 117·7° to 117·9° C., which they concluded to belong to the succinic acid series, and to have the formula $C_{20}H_{40}(COOH)_2$.

By repeatedly crystallising Japan wax from hot benzene, they finally separated a hard wax-like substance, melting at 43° to 45° C., and having an ester value of 252·6. They came to the conclusion that this wax-like substance was probably a mixed glyceride containing one molecule of Japanic acid and one molecule of palmitic acid.

Soluble Fatty Acids.—The soluble fatty acids (about 5 per cent. in quantity) were found to have the consistency of lard. Their acid value was 345·2, and their mean molecular equivalent 162. *Geitel* and *Want* considered that they were formed by the action of bleaching agents on the wax.

Unsaponifiable Matter.—The proportion of unsaponifiable matter found by *Geitel* and *van der Want* in four specimens varied from 1·48 to 1·63 per cent. This is a little higher than the amount found by *Allen* and *Thomson* (1·14 per cent.).

Glycerol.—A commercial sample examined by the present writer (*M.*) contained 7·2 per cent. of free fatty acids (as palmitic acid), and 10·9 per cent. of glycerol by Hehner's and the permanganate methods. The percentage of glycerol is much lower than that found by *Allen* in three samples (11·59 to 14·7 per cent.), a result which supported Berthelot's statement that Japan wax contained dipalmitin.

Properties and Tests of Purity.—Although possessing a wax-like appearance, from which it derives its name, Japan wax is as much a glyceridic fat as coconut oil or palm oil.

It is hard and brittle, and possesses a crystalline structure. When fresh it has a yellow to brown colour, but, on keeping, becomes coated with a fine white dust, which, examined under the microscope, is seen to consist of acicular crystals.

Specific Gravity.—According to *Kleinstück*[3] the specific gravity of recently-melted Japan wax is higher than the normal value, which, however, is gradually regained.

This is due to the fat possessing a greater expansion coefficient than water, as is shown by the following results obtained by *Kleinstück*:—

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[1] *Analyst*, 1896, xxi., 330.

[2] *J. prakt. Chem.*, 1900, lxi., 151.

[3] *J. Soc. Chem. Ind.*, 1890, ix., 1072.

Specific Gravity of Japan Wax Compared with that of Water at 40° C.

Temperature.	Japan Wax.		Water.
	Kept for some time.	Recently Melted.	
°C.			
4	...	...	1·00000
6·5	...	1·00237	0·99995
7·2	1·00737	...	0·99991
17·0	...	0·99123	0·99984
17·5	0·99846	...	0·99875
23·0	...	0·98747	0·99762
26·5	0·98615	0·98683	0·99764

Solubility.—Japan wax dissolves readily in benzene, ether, chloroform, and in boiling alcohol, from which it separates on cooling, forming a crystalline deposit. It is only sparingly soluble in petroleum spirit.

Detection of Adulteration.—*Tallow*, which is occasionally used to adulterate Japan wax, will be indicated by variations from the normal constants, and notably by the increase in the iodine value and decrease in the saponification value, and melting point of the fat and fatty acids.

According to *Dieterich*,[1] Japan wax has been considerably used of late years for adulterating South American ox-tallow. For its detection he recommends heating 26 grammes of the sample with 75 c.c. of petroleum spirit. The solution, on cooling, remains completely clear in the case of tallow, whilst a sample containing 5 to 10 per cent. of Japan wax does not yield a clear solution after long-continued heating, and remains opalescent in the presence of 1 per cent.

Borax Test.—This is also advocated by *Dieterich*:—On boiling 0·5 gramme of the fat with 20 c.c. of a saturated solution of borax, and then cooling the mixture, the aqueous layer is stated to remain perfectly clear and sharply separated from the fat, whilst in the presence of 5 per cent. of Japan wax the mass remains as an opaque white emulsion.

Starch.—*La Wall*[2] states that in America Japan wax is frequently adulterated with 20 to 25 per cent. of starch (usually maize starch). The addition can be detected by testing the freshly-fractured surface with iodine, and determined by treating the fat with chloroform, and washing the residual starch with ether and drying it at 100° C. Its amount can also be calculated from the lowering of the normal saponification value.

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[1] *Zeit. Nahr. Untersuch. Genussm.*, 1896, x., 330.

[2] *Amer. J. Pharm.*, 1897, lxix., 18.

Detection of Japan Wax in Beeswax.—Japan wax can be detected in beeswax by the presence of glycerol in the products of saponification, and by the ratio of the acid value to the ester value (*cf. Beeswax*).

KOKAM BUTTER.

Recorded Values.

Kokam Butter.

Specific Gravity.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Viscosity compared with Water at 140° F.	Refraction.		Melting Point.	Authority.
							Scale Divisions.	Refractive Index.		
At $\frac{100° C.}{100° C.}$ 0·8889	14·5	186·8	34·21	0·11	94·59	4·41	46·0	1·4565	° C. 42	Crossley & Le Sueur.[1]
At $\frac{40° C.}{15° C.}$ 0·8952	21·1	191·3	33·14	1·54	95·59	...	...	...	41-42	Heise.[2]
0·8574	...	...	...	...	...	...	...	...	...	,,

Fatty Acids.

Melting Point.	Solidification Point.	Molecular Equivalent.	Iodine Value of Liquid Acids.	Authority.
° C. 60-61	° C. 59·4	232	86·7	Heise.

This fat is obtained from the seeds of *Garcinia indica.* It is used in India as an edible oil and in the manufacture of soap. It closely resembles piney tallow in its chemical characteristics.

In the East Indies the natives separate the fat by boiling the crushed seeds with water, and purify it by filtration.

According to *Heise*, it consists, in the main, of oleo-distearin, which can be isolated in the same way as from Mkani fat (*q.v.*).

It is used for medicinal purposes and in the manufacture of soap, and, according to *Schädler*, has been employed as an adulterant of butter.

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[1] Crossley and Le Sueur, *J. Soc. Chem. Ind.*, 1898, xvii., 992.

[2] *Arbeit. aus. d. k. Gesundheitsamt.*, 1896, xiii., 302.

MACASSAR OIL.

Recorded Values.

Macassar Oil.

Specific Gravity at 15° C.	Saponification Value.	Hehner Value.	Reichert-Meissl Value.	Iodine Value.	Melting Point.	Solidification Point.	Authority.
					° C.	° C.	
0·924	213·4	...	...	53	22	...	Schädler.
0·924	230·0	91	...	53	22	...	Italie.
...	221·5	...	...	48·3	...	...	Lewkowitsch.
0·942	...	...	...	...	28	10	Glenk.
...	215·3	91·55	9	55	22	...	Wijs.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
° C.	° C. Dalican's Test.		
54-55	...	...	Schädler.
54-55	51·6-53·2	49·7-50·7	Lewkowitsch.
52-54	...	58·9	Wijs.
...	...	Liquid Acids. 103·2	

This fat is obtained by expression of the seeds of the East Indian tree, *Schleichera trijuga*. At the ordinary temperature it is a soft yellow mass, which melts to a clear yellow oil. According to *Schädler*,[1] it has a faint smell of bitter almonds, which is due to its containing about 0·05 per cent. of hydrocyanic acid.

It has acquired a great reputation as a hair restorative, but artificial mixtures are frequently substituted for it.

Schädler states that it contains 91 per cent. of insoluble fatty acids, including lauric and arachidic acids. *Wijs*[2] found the volatile acids to consist of acetic acid with a little butyric acid. The liquid fatty acids amounted to 55 per cent., and the unsaponifiable matter to 3·12 per cent. When treated with nitrous acid it is coloured orange-red and becomes viscous. It is readily saponified, yielding a hard white soap. It is only sparingly soluble in alcohol (*Glenk*)[3].

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[1] *Technologie der Fette*, 786.

[2] *Chem. Centralbl.*, 1900, i., 374.

[3] *Amer. J. Pharm.*, 1894, lxv., 528.

MAFURA FAT.

Recorded Values.

Mafura Fat.

Origin.	Saponification Value.	Iodine Value.	Melting Point.	Solidification Point.	Authority
			° C.	° C.	
...	...	...	42	36	Schädler.
I. Prepared in laboratory,	200·08	44·85	35-41	25-33	De Negri & Fabris.
II. Commercial, . .	220·96	46·14	35·5-42	30-37	,,
Fats from plants of same family as *Mafureira*,	195-239	45-72	10-31	...	,, [1]

Fatty Acids.

	Melting Point.	Solidification Point.	Iodine Value.	Authority.
	° C.	° C.		
I.	51-54	44-47	46·92	De Negri and Fabris.
II.	52-55	44-48	48·19	,,

This fat, which is used in the manufacture of soap, is expressed from the seeds of the plant, *Mafureira oleifera*.

It is a light yellow, tasteless fat, which melts to a brown oil on heating.

According to *De Negri* and *Fabris*,[1] it contains 71·4 per cent. of solid fatty acids and 23 per cent. of liquid fatty acids (oleic).

It causes a slight reduction in Becchi's test, and gives a brown coloration in the Baudouin test.

MARIPA FAT.[2]

Recorded Values.

Maripa Fat.

Specific gravity at $\frac{100° \text{C.}}{15·5° \text{C.}}$, ...	0·8686
Acid value, ...	31·09
Saponification value, ...	270·5
Hehner value, ...	88·9
Iodine value, ...	17·35
Melting Point, ...	26·5°-27° C.
Solidification Point, ...	25·5°-26° C.

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[1] *Zeit. anal. Chem.*, 1894, xxxiii., 571.

[2] *J. Soc. Chem. Ind.*, 1900, xix., 832.

Fatty Acids.

Specific gravity at $\frac{100° C.}{15·5° C.}$, ...	0·823
Melting point, ...	27·5°-28·5° C.
Solidification point, ...	25° C.

This fat is obtained from the fruit of *Palma maripa*, both by pressure and by boiling the fruit with water. The expressed oil, which is paler and of better flavour than that obtained by boiling, has a mild taste and faint odour. It is used in the West Indies as a substitute for butter.

MKANI FAT.

Recorded Values.

Mkani Fat.

Specific Gravity.	Acid Value.	Saponification Value.	Iodine Value.	Melting Point.	Solidification Point.	Authority.
° C.				° C.	° C.	
0·8926 at 40° 0·85606 at 100°	23·33	190·45	41·9	40-41	30·4-38	Heise.
0·9298 at 15° 0·8606 at 100°	11·6	186·6	41·0	liquid at 42°	turbid at 39°, liquid at 29·5°, temperature rising to 36° on solidification.	Henriques & Künne.
...	20·7	191·7	38 7	...	...	,,

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
° C.	° C.		
59	57·5	...	Heise.
61·5 complete	Dalican's Test. 61·4	42·1	Henriques and Künne.
...	61 6	...	,,

This fat is obtained from the East African tallow tree, *Stearodendron Stuhlmannii.* It is remarkable as being one of the first fats from which a mixed glyceride, oleo-distearin (*q.v.*), was isolated. It contains a large percentage of stearic acid and little or no palmitic acid.

According to *Henriques* and *Künne*, it would be a good substance for candle material, if it could be obtained in sufficient quantity

MOCAYA OIL.

Recorded Values.

Mocaya Oil.

Saponification Value.	Iodine Value.	Melting Point.	Solidification Point.	Melting Point of Fatty Acids.	Authority.
		° C.	° C.	° C.	
240·6	24·63	24-29	23-25	23-25	De Negri and Fabris.

This fat, which resembles coconut oil, is obtained from the seeds of *Acrocomia sclerocarpa*, a species of palm tree growing in Paraguay.

MOHAMBA SEED OIL.[1]

The seeds of this plant closely resemble I'Sano seeds, but yield much less oil (12 per cent.).

The oil is a yellow, odourless, and tasteless liquid, which does not solidify at − 15° C.

It has a specific gravity of 0·915 at 23° C., is slightly soluble in alcohol of 90 per cent. strength, and gives a rise of 55° C. in Maumené's test. According to *Hébert*, the fatty acids contain a white solid, unsaturated acid, which melts at 34° to 35° C., and absorbs the same amount of bromine as oleic acid, to which series it apparently belongs.

The liquid acids (about 90 per cent.) appear to consist, in the main, of oleic acid, judging by the bromine absorption and the result of the elaidin test. About 9 per cent. of glycerol is obtained on saponifying the oil.

MYRTLE WAX.

Recorded Values.

Myrtle Wax.

Specific Gravity.	Saponification Value.	Bromine Value.	Melting Point.	Solidification Point.	Authority.
			° C.	° C.	
0·995 at 15° C.,	205·5-211·7	...	40-44	39-43	Allen.
0·875 at $\frac{98^\circ\text{ C.}}{15{\cdot}5^\circ\text{ C.}}$,	...	...	...	...	,,
...	...	6·34	...	...	Mills.

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[1] Hébert, *Bull. Soc. Chim.*, 1896, xv., 935.

Fatty Acids.

Melting Point.	Solidification Point.	Molecular Equivalent.	Authority.
°C 47·5	°C. 46	243	Allen.

This fat is contained in the berries of different varieties of Myrica (*M. cerifera, carolinensis*, etc.), from which it is separated by boiling with water.

It is a wax-like substance of a greenish colour, and contains stearin, palmitin, myristin, and olein. *Allen* found 13·38 per cent. of glycerol in one specimen of the fat.

NUTMEG BUTTER.

Recorded Values.

Nutmeg Butter.

Specific Gravity.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Butyro-refractometer at 40° C.	Melting Point.	Authority.
0 990	22·4	154-159·6	...	...	...	°C. 51	Schädler.
0·945-0·996	17·2-44·8	134-178	40·1-52	...	...	38·5-51	Dieterich.
...	...	...	...	1·1-4·2	48·85	25-31·5	Spaeth.
0·990-0·995	...	...	31	...	...	45-51 47-48	Jean.

Fatty Acids.

Melting Point.	Solidification Point.	Authority.
°C. 42·5	°C. 40	Jean.

This fat is expressed from the seeds of *Myristica officinalis*, which is extensively cultivated in the East and West Indies, Brazil, etc. The nuts yield about 20 to 23 per cent. of a fat which contains a considerable proportion of essential oil (8 to 10 per cent.).

The glyceridic portion of the fat contains 40 to 45 per cent. of a solid fat (mainly myristin), and a fluid oil (*Schädler*).

According to *Jean*, the fat is composed of 73 to 74 per cent. of myristin, 20 per cent. of olein, 1 per cent. of butyrin, 3 per cent. of a resin, and 2 to 3 per cent. of essential oil.

The great variations in the chemical characteristics of different specimens of the fat are to be attributed to differences in the composition, some possessing a higher proportion of essential oil.

Nutmeg butter is a yellow, tallow-like fat with the characteristic odour and taste of the nut. It is used in medicine, and as a medium for the extraction of perfumes.

It dissolves completely in 2 parts of hot ether, and in 4 parts of hot alcohol. In cold alcohol only the colouring matter, essential oil, and liquid portion of the fat are soluble.

Jean states that nutmeg butter is sometimes adulterated with whale oil or sperm oil, and coloured with saffron or turmeric.

PALM OIL.

Recorded Values.

Palm Oil.

Specific Gravity.	Saponification Value.	Hehner Value.	Reichert Value.	Iodine Value.	Authority.
0·945 at 15° C.,	...	...	...	...	Schädler.
0·8586 at $\frac{98^\circ \text{C.}}{15\cdot5^\circ \text{C.}}$,	...	...	...	...	Allen.
...	...	95·6	...	...	Hehner.
...	...	...	...	51	Hübl.
...	...	...	...	51-52·4	Wilson.
...	202-202·5	...	...	...	Valenta.
...	...	...	0·5	...	Medicus and Scherer.

Fatty Acids.

Specific Gravity.	Melting Point.	Solidification Point.	Molecular Equivalent.	Iodine Value.	Authority.
	° C.	° C.			
0·8369 at $\frac{98^\circ \text{C.}}{15\cdot5^\circ \text{C.}}$,	50	45·5	270	...	Allen.
0·8701 at $\frac{100^\circ \text{C.}}{100^\circ \text{C.}}$,	...	...	...	...	Archbutt.
...	...	...	263	53·4	Williams.
...	...	42·5-43	...	...	Valenta

Source.—Palm oil is mainly obtained from the pulp of the fruits of the palm trees, *Elæis guineensis* and *melanococca*, the former growing in West Africa, and the latter in South America.

Many other species of palms, however, are now used as the source of the commercial product (see p. 629).

It is obtained either by expression or by leaving the fruit to decompose in holes, and collecting the oil as it rises to the surface.

Composition.—Palm oil contains palmitin, free palmitic acid, olein, and a small amount of linolin (*Hazura* and *Grüssner*). *Noerdlinger*[1] states that the solid fatty acids of palmitic acid (98 per cent.), stearic acid (1 per cent.), and heptadecylic acid, $C_{17}H_{34}O_2$ (1 per cent.), but the occurrence of the last requires confirmation.

Palm oil is remarkable for the large amount of free fatty acid that it contains. In the perfectly fresh oil it exceeds 10 per cent., whilst in commercial samples *Lewkowitsch* found from 50 to 70 per cent. of free acid, calculated as palmitic acid. This is due to enzymic hydrolysis of the fat before extraction.

Properties.—Palm oil varies in colour from orange-yellow to brown, and may be either in a semi-solid state, or as a hard mass. It has a sweet taste, and a characterictic pleasant odour, which is destroyed by chemical bleaching, but not by saponification with alkalis.

The colouring matter, which is readily removed by bleaching, is the cause of the colour reactions for palm oil given in older text-books.

Lewkowitsch states that the proportion of water and sand together should not exceed 2 per cent., and that commercial transactions are based upon this standard.

A table giving the proportion of neutral fat, water, and impurities, with the solidification points of the fatty acids of different commercial varieties of palm oil has been published by *de Schepper* and *Geitel.*[2]

For the valuation of palm oil for the soap and candle industries, Dalican's method of determining the solidification point of the fatty acids is commonly employed.

PALM-KERNEL OIL.

Recorded Values.

Palm-Kernel Oil.

Specific Gravity.	Saponification Value.	Iodine Value.	Reichert Value.	Hehner Value.	Melting Point.	Solidification Point.	Authority.
					° C.	° C.	
0·952 at 15° C.	..	..	..	..	27-28	20·5	Schädler.
0·91119 at $\frac{40° \text{ C.}}{15° \text{ C.}}$	..	..	2·4	..	..	..	Allen.
0·8731 at $\frac{99° \text{ C.}}{15° \text{ C.}}$	..	..	..	..	..	..	„
..	247·6	10·3-17·5	..	..	23-28	..	Valenta.
..	..	..	..	91·1	..	..	Lewkowitsch.
..	..	16-23	..	..	..	..	Ellis and Hall.

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[1] *J. Soc. Chem. Ind.*, 1892, xi., 445

[2] *Dingler's polyt. J.*, ccxlv., 295.

Fatty Acids.

Melting Point.	Solidification Point.	Saponification Value.	Molecular Equivalent.	Authority.
° C.	° C. Dalican's Test.			
25-28·5	..	258-265	211	Valenta.[1]
..	20·0-25·5	..	..	Lewkowitsch.

This fat is expressed from the seeds of the palms, the fruit of which yields palm oil.

It is a white or brownish coloured fat of somewhat softer consistency than palm oil.

According to *Oudemanns*,[2] it consists of triolein (26·6 per cent.), stearin, palmitin, and myristin (33 per cent.), and laürin, caprin, caprylin, and caproin (44·4 per cent.).

Ellis and *Hall*[3] have shown that the recorded iodine values are too low, and that the normal values range from 16 to 23. Oil extracted from the kernels appears to have a lower iodine value than expressed oil.

Elsdon,[4] using the method of alcoholysis (p. 143), separated the fatty acids as methyl esters, and found that palm-kernel oil had the following approximate percentage composition in comparison with coconut oil :—

Oil.	Caproic Acid.	Caprylic Acid.	Capric Acid.	Lauric Acid.	Myristic Acid.	Palmitic Acid.	Stearic Acid.	Oleic Acid.
Palm kernel,	2	5	6	55	12	9	7	4
Coconut, .	2	9	10	45	20	7	5	2

Noerdlinger[5] has published the results of a series of determinations, which show that the amount of oil contained in the kernels varies considerably with their origin. Thus, in the case of twenty-two samples obtained from different parts of West Africa, the average percentage ranged from 46·1 to 52·5.

The kernels exported to Europe are chiefly crushed at Harburg, but of late years the industry has been checked by the increased price of raw material, due to the abolition of slavery on the African coast.[6]

The fats from some of the more important palm trees of Brazilian origin have been described by *Bolton* and *Hewer*,[7] who give the following particulars of their characteristics :—

1. *Elæis guineensis.*—The fats of the pulp and kernel differ considerably from those of the corresponding African product.

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[1] *Zeit. angew. Chem.*, 1889, 334.

[2] *J. prakt. Chem.*, xi., 393.

[3] *J. Soc. Chem. Ind.*, 1919, xxxviii., 128 T.

[4] *Analyst*, 1914, xxxix., 78.

[5] *Zeit. angew. Chem.*, 1895, 19.

[6] *J. Soc. Chem. Ind.*, 1898, xvii., 618.

[7] *Analyst*, 1917, xlii., 35.

2. *Astrocaryum vulgare.*—The pulp oil is of pale straw colour and of the consistence of butter. Freshly expressed, it would be suitable for margarine.

3. *Astrocaryum Species.*—The kernel oil would be a suitable substitute for cacao butter and coconut " stearine."

4. *Acrocomia sclerocarpa*, which grows in the forests of Paraguay, yields a pulp oil resembling palm oil, but of less value. The kernel oil would be suitable for margarine.

5. *Maximiliana regia* (Anajá or kokerite palm) yields an odourless, firm white fat.

6. *Cocos syagrus.*—Two types of this tree are known, both producing similar fats.

7. *Attalea funifera* produces kernels with exceedingly hard shells. They yield a fat resembling coconut oil, but of softer consistence. It would be suitable for margarine.

8. *Œnocarpus batava.*—The oil from the pulp of this fruit closely resembles olive oil in its characteristics, and is particularly suitable for use as a salad oil.

Specimens of these fats had the following analytical values :—

Palm Oils.	Melting Point.		Solidification Point.	Saponification Value.	Refractive Index (Zeiss) at 40° C.	Iodine Value.	Free Fatty Acids as Lauric Acid in Kernel, and Oleic Acid in Pulp.	Unsaponifiable Matter.
	Beginning.	Complete.						
	° C.	° C.	° C.				Per cent.	Per cent
1. Pulp,	22-24·0	30-30·5	21·9	197·1	48·5-51·5	78·1-88·3	29·8-20·5	..
Kernel,	28·5-28·0	30·2-31·0	27·3-27·8	231·4-220·2	40·5-42·7	25·5-31·6	0·55-0·33	..
2. Pulp,	27·0	35·0	..	220·2	52·5	46·4	43·8	0·75
Kernel,	29·4-30·0	30·6-32·5	28·6	240-245·2	36·3-37·5	12·2-13·9	0·54-1·65	..
3. Kernel,	33	34	32·5	237·0	36·8	12·4	0·36	..
4. Pulp,	..	..	24·9	189·8	40·5	77·2	55·8	..
Kernel,	21	22-25·8	19·4-24·9	237-246	37·2-40·1	16-30	0·4-4·7	..
5. Kernel,	26	28·5	..	240·9	38·3	16·56	0·33	..
6. Blunt fruit, kernel.	23	29	26·8	252·5	37·4	12·5	3·2	..
Pointed fruit, kernel.	23	28·7	..	..	36·2	13·4	2·97	.. ..
7. Kernel,	22·2	26·1	22·7	246·9	37·1	16·3	2·80	..
8. Pulp,	..	..	7·0	191·8	52·5	78·2	0·48	1·1

Some of these fats are already extensively used as edible fats, whilst others will probably be used in this way before long. The close similarity in the characteristics of these palm fats makes it practically impossible to determine the origin of a given fat of this type. The most that can be said is that it belongs to a certain class of fats.

PINEY TALLOW. MALABAR TALLOW.

Recorded Values.

Piney Tallow.

Specific Gravity.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl. Value.	Hehner Value.	Refraction at 40° C.		Melting Point.	Authority.
						Scale Divisions.	Refractive Index.		
At 15° C.								° C.	
0·915	..	191·9	..	..	..	..	..	42	Höhnel & Wolfbauer
At $\frac{100^\circ \text{C.}}{100^\circ \text{C.}}$									
0·8907	5·18	189·29	39·63	0·44	95·21	47·5	1·4575	37·5	Crossley & Le Sueur.
0·8900	15·34	188·7	37·82	0·22	95·14	..	..	37	,,
0·915	..	191·9	..	..	..	..	..	40	Lemarié.

Fatty Acids.

Melting Point.	Solidification Point.	Authority.
° C.	° C.	
56·6	54·8	Höhnel and Wolfbauer.
57	..	Lemarié.

This fat is expressed from the seeds of the white dammer tree, *Vateria indica*, and is used in India for illuminating purposes and in the manufacture of soap. In the fresh condition it is of a greenish-white colour, but is rapidly bleached by the action of air and light.

The fat consists of about 75 per cent. of palmitin and about 25 per cent. of olein, and contains about 2 per cent. of a volatile oil (*Lemarié*).[1]

SAWARRI FAT.[2]

Recorded Values.

Sawarri Fat.

Specific gravity at $\frac{40^\circ \text{C.}}{15^\circ \text{C.}}$,	0·8981
Melting point,	29·5°-35·5° C.
Solidification point,	23·3°-29° C.
Hehner value,	96·61
Saponification value,	199·51
Reichert value,	0·65
Iodine value,	49·5

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[1] *Bull. Imp. Inst.*, 1903, (4), 206.

[2] Lewkowitsch, *J. Soc. Chem. Ind.*, 1890, ix., 844; *Proc. Chem. Soc.*, 1889, 69.

Fatty Acids.

Melting point, ...	48·3°-50° C.
Solidification point, ...	46°-47° C.
Mean molecular equivalent, . . .	272·8
Iodine value, ...	51·5
Acetyl value of liquid acids, . . .	14·03

This fat is obtained from "butter nuts," the nuts of *Caryocar tomentosum.*

Lewkowitsch found the solid fatty acids to consist chiefly of palmitic acid, whilst the liquid fatty acids contained oleic acid, and hydroxy acids which could readily be transformed into lactones.

SHEA BUTTER.

Recorded Values.

Melting Point.	Saponification Value.	Iodine Value.	Refractive Index (Zeiss).	Free Fatty Acids as Oleic Acid.	Unsaponifiable Matter.	Authority.
° C.			At 40° C.	Per cent.	Per cent.	
41·2	186·9	58·93	56·3	8·29	7·56	Revis and Bolton[1]

Shea butter, which is also known as karité butter, is derived from the seeds of a West African plant, *Butyrospermum* (or *Bassia*) *Parkii*, which, when expressed, yield about 40 per cent. of fat.

It is used locally as an edible fat, and is exported to Europe, where it is used as a constituent of a lard substitute, whilst the "stearine" or harder part of the fat is used as a chocolate fat.

Methods of removing part of the high proportion of unsaponifiable matter which characterises this fat have been introduced.

UCUHUBA FAT.

Recorded Values.

Ucuhuba Fat.

Saponification Value.	Iodine Value.	Hehner Value.	Melting Point.	Solidification Point.	Melting Point of Fatty Acids.	Authority.
			° C.	° C.	° C.	
219-220	9·5	93·4	39	...	46	Valenta.[2]
...	...	...	42·5-43	32-32·5	42·5-43	Noerdlinga.[3]

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[1] *Allen's Commercial Organ. Analysis*, ix., p. 148.

[2] *J. Soc. Chem. Ind.*, 1889, viii., 202.

[3] *Ber. d. d. chem. Ges.*, 1888, 2617.

This fat is contained in the nuts of *Myristica becuhyba*.

It is said to consist essentially of 89·5 per cent. of myristin and 10·5 per cent. of olein, together with a small amount of an essential oil.

It is a yellow-coloured fat, with a pleasant aromatic odour.

The fat from *Myristica surinamensis* is also sometimes described as Ucuhuba fat.[1] The seeds of this plant contain about 73 per cent. of fat, which melts at 36° C. (*Tschirch*) or 45° C. (*Reimer* and *Will*[2]), and has a very similar composition to the fat described above.

WILD OLIVE FAT.[3]

The seeds of a species of wild olive oil growing near Gatira, in San Salvador, yield, on extraction with solvents, a solid yellow fat, which melts at 30° C.

Hébert found this fat to contain more than 90 per cent. of solid white fatty acids (m.p., 48° to 49° C.), consisting of saturated and unsaturated acids in approximately equal proportion.

The unsaturated acids, separated by treatment of the lead salts with ether, melted at 44° to 45° C.

CLASS IX.—ANIMAL FATS.

BEEF FAT. (BEEF TALLOW.)

Recorded Values.

Beef Tallow.

Specific Gravity.	Saponification Value.	Hehner Value.	Reichert Value.	Iodine Value.	Melting Point.	Solidification Point.	Authority.
					°C.	°C.	
0·8950 at 15·5°C.,	...	..	...	...	...	...	Allen.
0·8626 at $\frac{98^\circ\ \text{C.}}{15{\cdot}5^\circ\text{C.}}$,	...	...	...	...	...	...	,,
...	...	...	...	35·6-38·9	47·6-48·5	...	Dieterich.
...	196 8	96·2	0·35	42·3	...	36	Mitchell.
...	195·7-200	...	..	35·4-36·4	...	...	Filsinger.

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[1] Tschirch, *J. Soc. Chem. Ind.*, 1887, vi., 676.

[2] *Ber. d. d. chem. Ges.*, 1888, 2011.

[3] Hébert, *Bull. Soc. Chim.*, 1896, xv., 935.

Fatty Acids.

Specific Gravity.	Melting Point.	Solidification Point.	Molecular Equivalent.	Iodine Value.	Iodine Value of Liquid Acids.	Authority.
	° C.	° C. Dalican's Test.				
0·8698 at $\frac{100^\circ\text{ C.}}{100^\circ\text{ C.}}$,	...	...	...	...	...	Archbutt.
...	...	...	270-285	...	...	Alder Wright.
...	...	37·9-46·2	284·5	...	...	Lewkowitsch.
...	45	...	...	42·5	...	Mitchell.
...	...	...	...	...	92·2 92·4	Wallenstein and Fink.

Beef fat is much more solid than lard, and, in a perfectly fresh state, is practically devoid of free fatty acids ; it has a neutral, bland taste. As in the case of the fat from the pig, sheep, etc., beef fat varies in consistency and chemical characteristics with the part of the animal from which it is derived, although to a much smaller extent than the other fats mentioned.

Composition.—It consists mainly of the glycerides of stearic, palmitic, and oleic acids, with traces of linolic and linolenic acids (*Farnsteiner*).

Various mixed glycerides have been isolated from beef fat, including oleodipalmitin, stearodipalmitin, oleopalmitostearin, and palmitodistearin.

According to *Lewkowitsch*[1] the ratio of stearin to palmitin is about 1 : 1 ; and this statement is borne out by the experiments of *Hehner* and *Mitchell*,[2] who found a specimen of pressed beef stearin to contain 50 per cent. of stearin, the remainder being mainly palmitin with traces of unsaturated glycerides.

The following table by *Leopold Mayer*[1] shows the variation in the composition of the fat taken from different parts of a Hungarian ox :—

Fat from	Fat.				Fatty Acids.				
	Melting Point.	Solidification Point.	Saponification Value.	Hehner Value.	Melting Point.	Solidification Point.	Saponification Value.	"Stearic" Acid Solidifying 54·8° C.	"Oleic" Acid Solidifying 5·4° C.
	° C.	° C.			° C.	° C.		Per cent.	Per cent.
Intestines,	50·0	35·0	196·2	95·7	47·5	44·6	201·6	51·7	48·3
Lungs,	49·3	38·0	196·4	95·4	47·3	44·4	204·1	51·1	48·9
Caul,	49·6	34·5	193·0	95·8	47·1	43·8	203·0	49·0	51·0
Heart,	49·5	36·0	196·2	96·0	46·4	43·4	200·3	47·5	52·5
Neck,	47·1	31·0	196·8	95·9	43·9	40·4	203·6	38·2	61·8
Groins,	42·5	35·0	198·3	95·4	41·1	38·6	199·6	33·4	66·8

On crystallisation from ether, beef fat yields a deposit of needle-shaped crystals arranged in characteristic fan-shaped bunches. On this fact, which is due to the presence of distinctive glycerides in the different fats, are based several tests for the detection of beef fat in lard (see *Lard*).

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[1] *Oils, Fats, and Waxes*, 1895, 482.

[2] *Analyst*, 1896, xxi., 328.

BUTTER FAT.

Recorded Values.

Butter Fat.

Origin.	Specific Gravity.	Acid Value.	Saponification Value.	Reichert-Meissl Value.	Hehner Value.	Iodine Value.	Refractometer.	Melting Point.	Authority.
...	...	...	225-230	...	...	28-32	1·445-1·448 at 60° C.	° C. 28-33	Thoerner.
English butter (68 samples),	0·9103-0·9117 at 39·5° C.	...	220·1-228·3	24·1-32·3	...	37·1-38·9	...	...	Richmond.
French (72 samples), .	0·9112-0·9116 at 39·5° C.	...	224·9-228·8	28·2-33·2	...	31·3-40·2	...	...	„
Mainly Guernsey cows (average of 40 samples),	0·9073 at $\frac{40° C.}{15·5° C.}$	0·50	228·5	28·3	87·65	33·35	...	33·2	Brown.
Dutch, 25 herds (363 samples, each representing mixed butter of 1 herd), . . .	0·9100-0·9128 at 37·8° C.	...	209·8-227·9	17·0-32·1	87·6 (lowest)	30·6-50·3	39·8 to 45·5 at 45° C.	...	Van Ryn.
Belgian (330 samples), .	0·864-0·868	...	...	26·07-34·5	85-89·6	...	40·2-40·7	...	Wauters.
Danish (monthly averages of 97 samples in 1899),	...	...	...	(*Wollny*) 26·9-30·8	...	...	39·9-41·8 at 45° C.	...	Stein.[1]
American (3 samples), .	...	...	...	...	...	36·86-41·2	...	33·5-36·1	Schweinitz & Emery.

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[1] Faber, *Analyst*, 1900, xxv., 201.

Insoluble Fatty Acids.

Origin.	Specific Gravity.	Melting Point.	Solidification Point.	Saponification Value.	Molecular Equivalent.	Iodine Value.	Refractive Index at 60° C.	Authority.
	° C.	° C.	° C.					
...	...	38-40	33-35	210-220	...	28-31	1·437 to 1·439	Thoerner.
Mainly Guernsey cows (aver. of 40)	0·9162 at $\frac{20°}{20°}$	41·7	...	214·5	261·0	...	...	Brown.
			Dalican's Test.					
Commercial,	...	...	39·2	...	...	30·2	...	Mitchell.
,,	...	...	33	...	...	34·25	...	,,

Soluble Fatty Acids.

Origin.	Specific Gravity.	Saponification Value.	Molecular Equivalent.	Authority.
Mainly Guernsey cows,	0·9479 at $\frac{20° C.}{20° C.}$	571·7	98·12	Brown.

Composition.—*Koefoed*[1] found a Danish butter to contain 91·5 per cent. of fatty acids, which he fractionated into the following constituents:—Oleic acid, together with acids of the formulæ $C_{15}H_{28}O_4$ and $C_{29}H_{54}O_5$, 34·0; stearic acid, 2·0; palmitic acid, 28; myristic acid, 22; lauric acid, 8·0; capric acid, 2·0; caprylic acid, 0·5; caproic acid, 2·0; and butyric acid, 1·5 per cent. Arachidic acid was not found.

Brown[2] examined a butter possessing the following characteristics:—Saponification value, 232·7; ester value, 232·5; iodine value, 29·28; molecular equivalent of insoluble fatty acids, 260·3, and molecular equivalent of soluble acids, 90·0.

The insoluble fatty acids were fractionally precipitated with magnesium acetate, and found to consist of:—Dihydroxystearic acid (calculated from acetyl value), 1·83; oleic acid, 32·50; stearic acid, 1·83; palmitic acid, 38·61; myristic acid, 9·89; and lauric acid, 2·57; total, 86·40 per cent. The soluble fatty acids were separated by the difference in their solubility in water at different temperatures. Calculated on the original fat, they gave the following results:—Butyric acid, 5·45; caproic acid, 2·09; caprylic acid, 0·49; and capric acid, 0·32 per cent.; total, 8·35 per cent.

The amounts of triglycerides of the total mixed acids were thus:—Dihydroxystearin, 1·04; olein, 33·95; stearin, 1·91; palmitin, 40·51; myristin, 10·44; laurin, 2·73; caprin, 0·34; caprylin, 0·53; caproin,

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[1] *Analyst*, 1892, xvii., 130.

[2] *J. Amer. Chem. Soc.*, 1899, xxi., 807.

2·32; and butyrin, 6·23 per cent. The proportion of oleic acid was calculated from the iodine value on the assumption that no other unsaturated fatty acid was present.

Farnsteiner obtained about 45 per cent. of elaidic acid from the liquid fatty acids of butter fat, and from this result calculated the proportion of oleic acid in the fat to be about 20 per cent. He also isolated a trace of an insoluble bromide with the characteristics of linolenic hexabromide, but could not separate the bromide of linolic acid.

The presence of hydroxy acids in butter, as found by *Brown*, is not in accordance with the conclusions of *Lewkowitsch*,[1] who was unable to detect them in different samples.

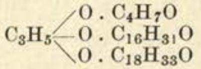
Bell calculated the composition of a sample of butter fat examined by him to be as follows:—Butyric acid (soluble fatty acids), 6·13; caproic, caprylic, and capric acids, 2·09; myristic, palmitic, and stearic acids, 49·46; oleic acid, 36·10; and glycerol, 12·54 per cent.

Similar analyses of 28 specimens of butter fat have been published by *Violette*.[2]

Stearic Acid.—The proportion of stearic acid in butter is, as a rule, very small. Thus, *Koefoed* found only 2 per cent., and *Brown* 1·8 per cent.; and their results are in agreement with the experience of *Hehner* and *Mitchell*,[3] who examined the fatty acids from a large number of specimens of butter by their method of determining stearic acid, and in most cases obtained no deposit, although in a few instances there was an appreciable amount.

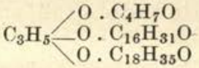
Using this method, *Holland*, *Reed*, and *Buckley*[4] found the insoluble fatty acids from various samples of butter fat to contain from 7 to 22 per cent. of stearic acid.

Mixed Glycerides.—There is considerable evidence in support of the theory that butter contains mixed glycerides. *Bell*[5] effected a fractionation of butter fat by treating it with hot alcohol. From 2 to 3 per cent. was dissolved, and on evaporating the solvent a fat melting below 15·5° C. was left, and this was found to contain 13 to 14 per cent. of soluble fatty acids and 79 to 80 per cent. of insoluble fatty acids. *Bell* concluded that this substance was a mixed glyceride, oleo-palmito-butyrin—



$$C_3H_5\begin{cases} O\,.\,C_4H_7O \\ O\,.\,C_{16}H_{31}O \\ O\,.\,C_{18}H_{33}O \end{cases}$$

Wynter Blyth and *Robinson*[6] also isolated a crystalline compound which they regarded as palmito-butyro-stearin—



$$C_3H_5\begin{cases} O\,.\,C_4H_7O \\ O\,.\,C_{16}H_{31}O \\ O\,.\,C_{18}H_{35}O \end{cases}$$

Henriques and *Künne*[7] have isolated insoluble chloro-iodides from butter and linseed oil, and as the analogous insoluble bromide obtained

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[1] *Oils, Fats, and Waxes*, 2nd Ed., 604.

[2] *J. Soc. Chem. Ind.*, 1890, ix., 1157.

[3] *Analyst*, 1896, xxi., 329.

[4] *J. Agric. Research*, 1916, vi., 101.

[5] *Chemistry of Foods*, ii., 44.

[6] *Proc. Chem. Soc.*, 1889, 5.

[7] *Ber. d. d. chem. Ges.*, 1899, xxxii., 387.

from linseed oil by *Hehner* and *Mitchell* is apparently the bromide of a mixed glyceride, it is highly probable that *Henriques* and *Künne* chloro-iodide from butter is also a compound containing a mixed glyceride (*cf. Mkani Fat*).

Brown,[1] however, considers that the evidence on the point is doubtful, for by separating butter fat into a more liquid and more solid portion by congealing it at a low temperature, and repeatedly crystallising the solid portion from chloroform, he obtained nearly pure tripalmitin, containing only traces of oleic, stearic, and other fatty acids.

On the other hand, *Amberger*[2] found that a sample of butter fat contained only 2·4 per cent. of triolein. By fractional crystallisation of hydrogenated butter fat he showed that the olein had been converted, not into tristearin, but into mixed glycerides. Butyric and caproic acid were also present as mixed glycerides. Among those isolated were butyro-diolein, butyropalmito-olein, and oleo-dipalmitin.

Proximate Composition of Butter.—*Vieth*[3] obtained the following results from the analysis of butter of different origin :—

Butter.	Fat.	Curd.	Salt.	Water.
English (72), ...	86·85	0·59	1·02	11·54
French, fresh (108), . . .	84·77	1·38	0·09	13·76
,, salted (5), . . .	84·34	1·60	2·01	12·05
Kiel, ,, (40), . . .	85·24	1·17	1·35	12·24
Danish, ,, (17), . . .	83·41	1·30	1·87	13·42
Swedish, ,, (25), . . .	83·89	1·33	2·03	13·75

The following table, compiled from *Richmond's* figures,[4] shows the average percentage composition of butter of different origin in 1894 :—

Origin.	Water.	Fat.	Solids not Fat.	Salt.	Ratio of Water to Solids not Fat, less Salt.
French, fresh, 41 samples, . .	13·60	85·05	1·35	0·09	9·2
,, salt, 31 ,, . .	11·27	85·28	3·45	1·97	13·1
Brittany, 6 ,, . .	14·26	83·84	1·90	0·16	12·2
English, fresh, 22 ,, . .	13·49	85·70	0·81	0·14	5·0
,, salt, 46 ,, . .	13·11	83·94	2·95	2·11	6·4
Australian and New Zealand, salt, 6 samples, ...	10·72	87·21	2·07	1·23	7·9

The average results of the analysis of 300 samples of butter made by *König*[5] were as follows :—Water, 13·59 ; fat, 84·39 ; casein, 0·74 ; milk-sugar, 0·50 ; lactic acid, 0·12 ; and salts, 0·66 per cent.

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[1] *J. Amer. Chem. Soc.*, 1899, xxi., 807.

[2] *Zeit. Unters. Nahr. Genussm.*, 1918, xxxvi., 313.

[3] *Analyst*, 1891, xvi., 1.

[4] *Ibid.*, 1895, xx., 55.

[5] *Chem. menschl. Nahr. Genussm.*, ii., 300.

Water in Butter.—The proportion of water left in the butter will naturally vary with the method of manufacture. At one time there was no legal standard as to the amount, but 16 per cent. is fixed as the highest limit for genuine butter.

Richmond[1] considers that, as a rule, the nearer the percentage of water to 13·5 the better the quality of the butter. In 1896 he found the average amount in butters examined by him throughout the year to be as follows :—

	Per cent.
English, fresh, ...	13·82
,, salt, ...	13·94
French, fresh, ...	14·40
,, salt, ...	12·2

In a previous communication *Richmond*[2] described the results of experiments, which showed that salt butter loses water rapidly at first during the first few days after churning, but that the proportion becomes practically constant towards the end of the following week. In his opinion there is no foundation for the belief that salt butter contains more water than fresh butter.

The following table, showing the amounts of water found by *Estcourt*[3] in 250 samples of butter examined in 1899, is interesting as indicating the variation in the produce of different countries :—

Origin.	Number of Samples.	Average Percentage of Water.	Highest Percentage of Water.	Lowest Percentage of Water.
Finnish, ...	85	12·3	18 0	8·0
Danish, ...	89	13·5	18·0	9·0
Irish, ...	39	14·1	20·0	9·0
Swedish, ...	14	13·75	17·8	11·8
Canadian, ...	10	13·2	19·4	10·0
German, ...	8	13·5	14·8	11·4

Estcourt considers that the proportion of water in Irish butter need not be high if proper care be taken.

Faber[4] states that the results of analyses made in connection with the State Butter Shows in Copenhagen show a yearly average of 13·93 to 14·32 per cent. of water on 12,093 samples of Danish butter examined between 1890 and 1898.

Abnormal Butter.—A Belgian commission appointed to investigate the composition of butter in that country, found that abnormal samples were usually derived from small dairies ; that these abnormal results were of most frequent occurrence from August to December ; and that they disappeared during the months of March, April, and May.

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[1] *Analyst*, 1897, xxii., 94.
[2] *Analyst*, 1896, xxi., 90.
[3] *Ibid.*, 1900, xxv., 114.
[4] *Analyst*, 1900, xxv., 199.

Effect of Late Stalling.—The abnormal character of Dutch butter has been repeatedly shown to coincide with the end of the pasturage season, and after stalling the cows it speedily becomes normal. This is illustrated by the following table,[1] showing the composition of the butter from the milk of a herd of seven cows at different periods. The cows were stalled on 22nd October :—

Date.	Refractometer at 45° C.	Specific Gravity at 37·8° C.	Reichert-Meissl Value (*Wollny*).	Hehner Value.	Volatile Fatty Acids.	Saponification Value.	Iodine Value (*Hübl*).
					Per cent.		
Sept. 11,	44·5	0·9114	24·4	89·9	4·4	216·9	44·9
,, 25,	45·1	0·9109	21·1	90·5	4·0	218·1	47·2
Oct. 2,	45·0	0·9102	20·3	90·6	4·0	214·2	49·1
,, 9,	44·6	0·9108	19·7	90·7	3·9	214·5	47·5
,, 16,	45·0	0·9112	20·3	90·6	4·0	215·9	48·8
,, 23,	45·3	0·9113	19·0	90·7	3·8	212·0	49·2
Nov. 6,	42·6	0·9108	21·5	90·3	4·0	218·3	41·9
,, 20,	42·3	0·9112	23·1	90·1	4·2	209·0	44·5
Dec. 11,	40·2	0·9111	25·4	89·2	4·9	224·5	34·2

Influence of Food.—The effect of feeding cows upon different kinds of fats has been shown by the experiments of *Baumert* and *Falke*.[2] A Swiss and a Dutch cow were fed for five periods of twenty days each upon hay and rape meal, to which was added during three of the periods sesamé oil, coconut oil, and almond oil.

The effect of these oils upon the butter was as though the butter had been subsequently mixed with them. This is shown in the following average results :—

Dutch Cow.	Oleo-refractometer.	Saponification Value.	Reichert-Meissl Value.	Iodine Value.	Melting Point.
					° C.
I. Rape meal & hay, ...	+ 2·4	223	29·5	45·0	33·96
II. ,, ,, ,, + sesamé oil, .	+ 5·4	206	15·7	52·9	36·76
III. ,, ,, ,, + coconut oil,	− 0·6	230	18·6	35·2	34·76
IV. ,, ,, ,, + almond oil, .	+ 4·3	207	15·3	53·9	34·50
V. ,, ,, ,, alone, . .	+ 3·6	216	24·4	44·5	35·15
SWISS COW.					
I. Rape meal & hay, ...	+ 1·7	224	31·0	44·3	34·16
II. ,, ,, ,, + sesamé oil, .	+ 5·6	204	16·9	53·9	37·00
III. ,, ,, ,, + coconut oil,	− 0·5	237	20·0	37·1	33·58
IV. ,, ,, ,, + almond oil, .	+ 3·6	210	19·7	50·9	34·28
V. ,, ,, ,, alone, . .	+ 3·0	218	22·0	41·2	34·50
FATS USED.					
Sesamé oil, ...	+ 17·6	190	0·4	116	...
Coconut oil, ...	− 9·2	255	8	9	...
Almond oil, ...	+ 13·6	195	0	98	...

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[1] Van Ryn, *loc. cit.*, 32.

[2] *Zeit. Untersuch. Nahr. Genussm.*, 1898, i., 665.

The sesamé oil reaction was not given by the butter from the milk of cows fed with sesamé oil.

Brown (*loc. cit.*) finds that certain kinds of food, such as gluten meal, tend to lower the saponification value and increase the iodine value, whilst other kinds, such as beets, mangels, and other roots have the opposite effect.

Ruffin[1] has made a similar series of experiments to determine the influence of the nature of the food on the analytical values of butter fat, and summarises his results in the following table :—

Food of Cows.		Refractometer Reading.	Saponification Value.	Reichert-Wollny Value.
Fodder, lucerne, &c.,	Max.,	33	232	34·9
	Min.,	30	224	27·6
Cotton-seed oil-cake,	Max.,	30	228	29
	Min.,	28·5	222	26·4
Cotton-seed oil-cake and fodder,	Max.,	30	229	30
	Min.,	29·5	221	28·4
Earth-nut oil-cake,	Max.,	31	228	29
	Min.,	30	225	26·4
Earth-nut oil-cake and fodder,	Max.,	30	229	32
	Min.,	28	221·9	28
Coconut cake,	Max.,	33	240	31
	Min.,	32	231	28·5

Ledent[2] confirms the conclusion that butter fat from the milk of cows fed upon coconut oil shows indications of the presence of that fat.

Rancidity of Butter.—*Brown's*[3] experiments show that with the development of rancidity there is a decided increase in the acid, saponification, and Reichert values, and a decrease in the percentages of insoluble fatty acids and glycerol.

The specific gravity, which ranged from 0·9050 to 0·9102 at $\frac{40^\circ\text{ C.}}{15{\cdot}5^\circ\text{ C.}}$ in fresh butter-fat, increased to 0·9195 to 0·9252 on becoming rancid.

In the earlier stages of rancidity the melting point showed an increase of 0·1° C. to 1·0° C., and in some cases the fat showed the phenomenon of double melting point. Thus a sample of rancid fat, melting at 24·2° C., when kept at that temperature for a few minutes solidified, and then did not melt until 33·4° C. When the fat became more rancid, it ceased to show this phenomenon. *Brown* considers that this may be due to the presence of two classes of decomposition products such as aldehydes and oxy-acids.

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[1] *Ann. de Chim. anal.*, 1899, iv., 383.

[2] *Bull. Soc. Chim. Belg.*, 1913, xxvii., 325.

[3] *J. Amer. Chem. Soc.*, 1899, xxi., 975.

The critical temperature of solution was found to be 57° C. with fresh butter; and 45° to 50° with rancid butter fat, according to the degree of acidity. The mean refractive index at 30° C. was 1·45897 for fresh butter, and 1·45987 for rancid fat. The change in the chemical composition and heat of combustion is shown in the following table :—

	Carbon.	Hydrogen.	Oxygen.	Calories.
	Per cent.	Per cent.	Per cent.	Per gramme.
Fresh butter fat, . .	75·17	11·72	13·11	9366
Rancid ,, ,, . .	73·88	11·57	14·55	9095

The changes taking place in a butter that had been kept for six years are shown by the following results of *Allen* and *Moor* :—[1]

Danish Butter.	Specific Gravity at 100° C.	Reichert-Wollny Value.	Saponification Value.	Soluble Acids.	Insoluble Acids.	Iodine Value.
				Per cent.	Per cent.	
1888	0·8639	22·63	222·7	4·37	90·24	...
1894 (3 portions)	0·8634 to 0·8730	12·02 to 14·43	219·9 to 228·8	3·82 to 5·60	90·0 to 90·73	25·1 to 30·0

Clayton[2] gives the following figures obtained in the examination of a butter eighteen years old. When fresh this sample had a Hehner value of 87·75, and contained the normal proportion of water, salt, and curd :—

Specific Gravity at $\frac{100° \text{ C.}}{15·5° \text{ C.}}$	Melting Point.	Hehner Value.	Reichert-Meissl Value.	Saponification Value.	Acidity.
	° C.				
0·8742	33	85·72	22·36	256·8	100 grammes required 160·3 N—KOH.

Characteristics of Butter Fat and Tests of Purity.

Specific Gravity.—As a rule, this shows little variation whatever the origin of the butter. In some cases it may afford an indication of the presence of foreign fats, since butter possesses a greater density than other animal fats. Coconut oil and palm-kernel oil, however, resemble it closely in this respect.

Relationship between Specific Gravity and Insoluble Fatty Acids.—There is, in general, a correspondence between these values in the case of butter and animal fats, whilst the presence of vegetable oils,

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[1] *Analyst*, 1894, xix., 129.

[2] *Analyst*, 1898, xxiii., 36.

such as sesamé, coconut, or cotton-seed oils, which have a higher specific gravity than animal fats, is shown by a deviation from this ratio.

Leonard[1] found that this relationship might be represented by the formula,

$$y = k\,(1 - x),$$

where y represents the percentage of insoluble fatty acids, x the specific gravity at $\frac{38^\circ \text{ C.}}{15{\cdot}5^\circ \text{ C.}}$, and k a constant with the mean value of $951 \pm 1{\cdot}8$.

For practical purposes, the following formula is sufficient :—

$$y = 951\,(1 - x).$$

In only 3 cases out of 63 samples examined by *Leonard* was there a difference of more than 1·4 per cent. between the amounts of insoluble fatty acids calculated by the formula and actually determined, whilst in 35 cases the agreement was within 0·5 per cent.

Hehner Value.—*Hehner* was the first to correct the idea that butter only contained a small proportion of volatile fatty acids. He determined the amount of the insoluble acids in a very large number of samples, and found that the average quantity was 87·5 per cent., the limits being 86·5 and 88 per cent.

Other values recorded are 85·5 to 89·9 (*Bell*) and 85·8 to 89·7 (*Vieth* and *Fleischmann*). In the case of abnormal Dutch butter, considerably higher values have been found (*vide supra*).

As considerable difficulty is sometimes experienced in washing out the whole of the higher soluble acids, the Reichert value is, as a rule, determined instead of the Hehner value, since, in most cases, it affords as reliable information in a much shorter time.

Reichert Value.—The presence of so large a proportion of volatile fatty acids distinguishes butter fat from the body fat of animals and from most vegetable fats, coconut oil and palm-kernel oil being the only well-known oils giving considerable Reichert values.

The formula used to calculate the proportion of added fat in butter from the Reichert-Meissl value is

$$\text{B} = \frac{100\,(n - \text{C})}{28{\cdot}78 - \text{C}},$$

where n represents the value of the sample and C that of the foreign fat, whilst 28·78 represents the average Reichert-Meissl value of pure butter.

Unfortunately this value is by no means constant, but varies with the kind of cows, with their food, with the season, and with the time since calving. Hence, any exact calculations based upon an average value are fallacious.

Brown gives the ordinary limits of the Reichert-Meissl value of

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[1] *Ibid.*, 1898, xxiii., 282.

pure butter as 20 to 33, the extreme limits recorded being 11·2 (*Morse*) and 41 (*Nilson*).

Richmond[1] obtained the following results (Reichert-Wollny) with samples of different origin in 1893:—French butter, fresh, 25·4 to 30·8; French butter, salt, 26·2 to 32·8; New Zealand butter, salt, 32·1 to 32·8.

The *Reichert Values* of 250 samples examined by *Estcourt*[2] showed the following variations:—

Origin	Number of Samples.	Average Reichert Value.	Highest Reichert Value.	Lowest Reichert Value.
Finnish, . .	85	13·8	17 6	11·9
Danish, . .	90	15·2	17·0	12 5
Irish, . .	39	14·0	15·5	12·8
Swedish, . .	14	14·4	16·2	13·7
Canadian, .	10	14·1	15·5	13·0
German, . .	8	15·3	16·2	13·5

The values obtained by *Thorpe*[3] with 357 samples of English butter fat ranged from 22·5 to 32·6.

The effect of the period of lactation upon the *Reichert-Meissl* value was demonstrated by *Vieth*, and subsequently by *Kreit*,[4] who examined 37 samples of butter at different periods throughout the year and obtained results ranging from 21·1 to 34·4, whilst in every instance the figures above 30 were given by the butter from cows that had recently calved.

The influence of exposure to bad weather and cold is manifestly the explanation of the abnormally low Reichert-Meissl values of the butter of cows that have been left in pasture to a late period of the year.

This has been clearly shown by the experiments of *Vieth*, *Reichert*, and others, and most recently by the results obtained by *van Ryn*,[5] the Reichert-Meissl values invariably beginning to rise shortly after the cows had been stalled towards the end of October. Thus the average values of 428 samples of butter from the milk of different herds were—

September, . .	24·8	November, . .	25·2
October, . .	23·7	December, . .	26·6

Of these samples, three had values of 17 to 18·9, three of 19 to 19·9, and eight of 20 to 20·9; whilst 50 per cent. were below 25. Nine samples gave values of 29 to 29·9 and five from 30 to 33.

The following results given by *Thorpe* (*loc. cit.*) show the variations

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[1] *Analyst*, 1893, xviii., 52.

[2] *Ibid.*, 1900, xxv., 115.

[3] *J. Chem. Soc.*, 1904, lxxxv., 254.

[4] *Analyst*, 1893, xviii., 134.

[5] *Loc. cit.*, 14.

which may take place in this value at different times of the year. All the samples were of British origin :—

	May.	June.	July.	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	April.
Minimum,	26·5	26·0	22·5	23·4	22·4	22·3	23·3	23·9	25·6	22·0	27·1	25·3
Maximum,	32·8	32·8	31·4	30·5	29·5	29·6	32·9	30·4	31·0	31·6	34·3	33·1

The influence of different oils in the food upon the Reichert value is shown by the results of *Baumert* and *Falke* given in the table (*supra*).

Official Method of Determining Butter Fat in Margarine.—A Committee of the Society of Public Analysts in conference with Dr. Thorpe have made a report on Section 8 of the Food and Drugs Act, 1899, which enacts that the proportion of butter fat in margarine shall not exceed 10 per cent.

This Committee recommended—1. That the proportion of butter fat should be calculated from the amount of volatile fatty acid ascertained by Wollny's modification of the Reichert-Meissl process.

2. That no presumption should be raised against margarine, as regards the amount of butter fat, unless the Reichert-Wollny figure exceeded 4.

3. That the proportion of butter fat should be assumed to be as follows :—

Reichert-Wollny Value of the Mixture.	Proportion of Butter Fat in the Mixture.
4·0	10
4·3	11
4·6	12
4·9	13
5·2	14
5·5	15
5·9	16
6·2	17
6·5	18
6·8	19
7·1	20

The Reichert-Wollny method recommended by the Committee is as follows :—" Five grammes of the liquid fat are introduced into a 300 c.c. flask, with a neck 7 to 8 centimetres in length and 2 centimetres in width. Two c.c. of a solution of caustic acid (98 per cent.) in an equal weight of water—preserved from the action of atmospheric carbonic acid—and 10 c.c. of alcohol (about 92 per cent.) are added, and the mixture is heated under a reflux condenser, connected with the flask by a T-piece, for fifteen minutes in a bath containing boiling water. The alcohol is distilled off by heating the flask on the water-bath for about half an hour, or until the soap is dry. One hundred c.c. of hot water, which have been kept boiling for at least ten minutes, are added, and the flask heated until the soap is dissolved. Forty c.c. of normal sulphuric acid and three or four fragments of pumice or broken pipe stems are added, and the flask is at once connected with a condenser by means of a glass tube 7 millimetres wide and 15 centimetres from the top of the cork to the bend. At a distance of 5 centimetres above the cork is a bulb 5 centimetres in diameter. The flask is supported on a circular piece of asbestos 12 centimetres in diameter, having a hole in the centre 5 centimetres in diameter, and is first heated by a very small flame to fuse the insoluble fatty acids, but the heat must not be sufficient to cause the liquid to boil. The heat is increased, and when fusion is complete 110 c.c. are distilled off into a graduated flask, the distillation lasting about thirty minutes (say twenty-eight to thirty-two minutes), the distillate is shaken, 100 c.c. filtered off, transferred to a beaker, 0·55 c.c. of phenol-phthalein solution (1 gramme in 100 c.c. of alcohol) added, and the filtrate titrated with deci-normal soda or baryta solution. Precisely the same procedure (with the same reagents), omitting the fat, should be followed, and the amount of deci-normal alkali required to neutralise the distillate ascertained. This should not exceed 0·3 c.c. The volume of deci-normal solution of alkali used, less the figure obtained by blank experiment, is multiplied by 1·1. The number so obtained is the Reichert-Wollny number."

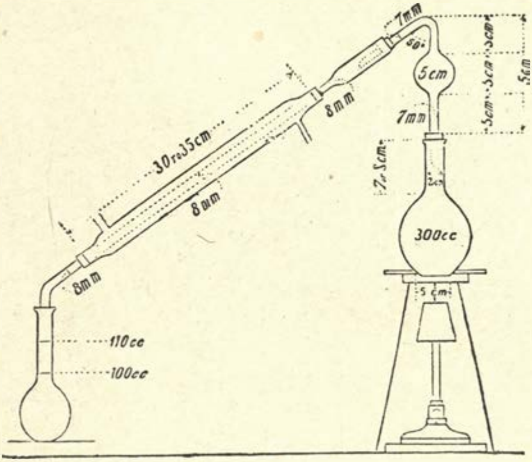

Fig. 103*a*.—Reichert-Wollny Apparatus.

"*Notes on the Method*.—The sample is melted and filtered from curd and water through a dry filter. From the filtrate the 5 grammes of fat for the purpose are taken. The soda solution is filtered clear from carbonate formed in its preparation, and kept in a special bottle. The Soxhlet spherical condenser is a convenient one for the reflux distillation. This is fixed near the water-bath in which the saponification is to take place, and is connected with the flask by means of a T-piece and india-rubber tubes inclined at an angle of 45°. During the saponification the free limb of the T-piece is directed upwards, and its end closed by a short piece of india-rubber and glass rod. At the end of fifteen minutes this limb is turned downward and the piece of glass rod replaced by a tube carrying away the alcohol.

"One hundred c.c. of hot distilled water are added, and the flask frequently shaken until the soap is dissolved. The Liebig is a convenient form of condenser. One containing a column of water, 30 to 35 centimetres in length, gives sufficient condensing surface. After shaking the distillate, about 5 c.c. are filtered through a dry paper into 100 c.c. flask. This serves to wash out the flask. When the 100 c.c. are transferred to a beaker, the flask is not washed out, but the main quantity is neutralised with the standard solution of alkali and returned to the flask, then again transferred to the beaker and the titration completed."

This method is the one in use in the Government Laboratory, and has been officially adopted by the Society of Public Analysts.[1]

In a further Report[2] the Committee recommended the addition of the following words to their original Report:—"The limiting figure of 4 obtained by the Reichert-Wollny method described, and the table of figures connected therewith, are not applicable to those margarines in which the insoluble volatile acids number exceeds 1."

The Valenta Test.—*Chattaway*, *Pearmain*, and *Moor*[3] examined twenty-four samples of butter fat and five samples of margarine by their method of applying the test (*cf.* Chap. IV.), with the following results:—

	Maximum.	Minimum.	Mean.
	° C.	° C.	° C.
Butter fat, . .	39·0	29·0	36·0
Margarine, . .	97·0	94·0	95·5

They also showed that the composition of mixtures of butter and margarine of known values could be calculated from the results of this test.

Jones[4] recommends the standardisation of each fresh lot of acetic acid on a filtered sample of normal butter fat kept in a bottle. The acid is tried with this fat, and diluted with water until the turbidity temperature is 60° C. He finds the turbidity temperature of butter fat (3 c.c. of fat and of acid) to vary from 40° C. to 70° C., the usual figures being 52° C. to 65° C.; whilst margarine gives temperatures of 95° C. to 106° C., generally from 100° C. to 102° C.

The following analyses by *Jones* show the relationship between the turbidity temperature and chemical composition of different samples of butter fat:—

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[1] *Analyst*, 1899, xxv., 309-313.

[2] *Ibid.*, 1909, xxxiv., 514.

[3] *Ibid.*, 1894, xix., 147.

[4] *Ibid.*, 152.

Turbidity Temperature, ° C.	54	56	55	60	55	56
Saponification value,	226·8	224·0	226·2	220 0	223·4	226·2
Soluble acids, per cent.,	5·14	4·79	5·19	4·19	5·02	5 30
Insoluble acids, ,,	88·92	89·30	89·04	90·28	89·08	88·78
Reichert-Wollny value,	27·2	25·6	28·1	22·5	26·7	28·2
Equal to volatile acids as butyric acid, per cent.,	4·79	4·50	4·95	3·96	4·69	4·97

Turbidity Temperature, ° C.	57	41	45	59	48
Saponification value,	225·1	224·5	225·7	217·8	221·2
Soluble acids, per cent.,	5·20	4·97	5·05	4·12	4·98
Insoluble acids, ,,	89·11	88·74	88·56	90·18	88·73
Reichert-Wollny value,	28·1	26·7	27·2	22·2	25·4
Equal to volatile acids as butyric acid, per cent.,	4·95	4·69	4·79	3·91	4·47

In *Jean's*[1] method of applying the Valenta test 3 c.c. of the fat or oil are shaken with 3 c.c. of glacial acetic acid (sp. gr. 1·0565 at 15° C.) in a tube graduated in tenths of a c.c., and the tube placed in a water-bath at 50° C. until the layers separate. The percentage of acid dissolved by the fat is then obtained by subtracting the amount of the acid layer from 3 and multiplying by 3·33.

In this way the following results were obtained :—Butter, 63·3 to 70 per cent. ; maize, castor, coconut, and mineral oils, 100 per cent. ; cameline, nut, olive, earth-nut, neats-foot, palm, almond, poppy, radish, and rape-seed oils, 30 to 43·7 per cent. ; margarine, 26·7 to 40 per cent. ; and tallow, 26·7 per cent.

The following table shows the figures obtained with samples of butter of different origin :—

Origin of Butter.	Oleo-refractometer Reading.	Solubility of Acetic Acid.	Reichert-Wollny Value.
		Per cent.	
Normandy, pure,	−30	63·33	29·25
Rennes, ,,	−29	63·33	27·5
Touraine, ,,	−35	73·0	31·42
Brittany, suspicious,	−25	60·0	24·7
Ardennes, ,,	−27	58·33	...
Indre-et-Loire, suspicious,	−26	56·66	25·75
Rennes, salt, adulterated,	−25	60·0	23·98
,, suspicious,	−25	60 0	...
Brittany, ,,	−25	60·0	22·99
Rennes, ,,	−26	60·0	22·0
Brittany, salt, suspicious,	−25	60·0	23·65
Isigny + 10 per cent. coconut oil,	−33	66·66	26·8
,, + 15 ,, ,,	−34	90·0	...
,, + 28	−36	96·0	24·13
,, + margarine,	−24	53·0	...

See also pp. 74-77.

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[1] *Analyst*, 1892, xvii., 194.

Crystallisation.—*Zega*[1] recommends a method of crystallising the fat from a mixture of six parts of ether, four of alcohol, and one of glacial acetic acid. One c.c. of the melted fat is dissolved in 20 c.c. of the hot solvent, which is then allowed to cool at 15° C. to 18° C. In the case of pure butter only a slight deposit is obtained after one to one and a half hours, whilst margarine gives a deposit in a few minutes, and mixtures containing 10 per cent. of margarine begin to separate within fifteen minutes.

Examined under the microscope the crystals from pure butter are seen to consist of long rods converging to the centre and forming stars, whilst margarine crystals are minute needles closely packed into sheaves or circles.

Solubility in Alcohol.—*Polenske*[2] bases a test for foreign fats upon the greater solubility of butter fat in absolute alcohol at 18° C. In this way a fractionation of the fat is effected, and by determining the Reichert-Meissl values of each portion, more valuable results can be obtained than from the whole fat.

Polenske finds that a low Reichert-Meissl value is accompanied by a slight solubility, although a small solubility is not always associated with a lower Reichert-Meissl value of the more soluble portion.

Critical Temperature of Solution.—This affords a rapid test of the purity of butter, although, as is the case with other tests, it cannot be regarded as conclusive by itself.[3]

The following comparative results were obtained by *Crismer*[4] with ten commercial samples of butter, the determinations being made in sealed tubes with alcohol of specific gravity 0·8195 at 15·5° C. :—

No.	Manner of Fusion.	Specific Gravity at 100° C.	Refractometer Reading.	Hehner Value.	Reichert-Meissl Value.	Critical Temperature. ° C.
1	Clear,	0·866	– 33	87·65	...	100·0
2	Turbid,	0·864	– 23	90·19	20·6	106·5
3	Clear,	0·867	– 33	85·60	...	90·0
4	,,	0·866	– 33	87·24	...	96·0
5	,,	0·8655	– 30	88·33	27·9	99·0
6	,,	0·866	– 33	86·82	...	96·5
7	,,	0·866	– 32	87·44	...	99·0
8	,,	0·8665	– 34	87·46	...	99·0
9	,,	0·866	– 34	86·25	...	95·0
10	,,	0·866	– 30	87·96	...	97·2

Sesamé oil was detected in the second sample.

In a subsequent communication *Crismer*[5] has shown that an open tube can be used instead of sealed tubes, provided that the critical temperature does not exceed 78° C. About 0·5 gramme of the filtered fat is mixed with about 1 c.c. of absolute or nearly absolute alcohol in

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[1] *Chem. Zeit.*, 1899, xxiii., 312.

[2] *Analyst*, 1895, xx., 277.

[3] See p. 72.

[4] *Bull. de l'Ass. belge Chim.*, 1895, ix., 5.

[5] *Ibid.*, 1897, x., 312, 453.

a tube 7 to 8 cm. in length by about 1 cm. in diameter. The tube is closed by a cork, through which passes a thermometer, with its bulb entirely covered by the liquid. This tube is gently heated in a larger tube, the contents being shaken vertically until they become homogeneous. The temperature at which they separate again on cooling is the critical temperature.

The results thus obtained correspond with those given by the sealed tube method, as is shown by the following comparative figures :—

With Alcohol, Specific Gravity 0·7976 in Open Tube.	With Alcohol, Specific Gravity 0·8195 in Sealed Tube.	Difference.
Butters (8), 50-54·8, . . .	95·5-102·5	45·5-46
Margarine & mixtures, 63·8-78,	109-24	45·2-46

Old and rancid butter gives a considerably lower value than fresh butter, but on neutralising such samples with sodium carbonate, and washing the fat with hot water, they show the normal critical temperature.

The critical temperature of neutralised butter is that of the acid butter plus the number of c.c. of $\frac{N}{20}$ alcoholic alkali required to neutralise 2 c.c. of the butter fat.

The mean critical temperature for 173 samples of butter fat examined during twelve months was 52·5, or 55·5 after neutralisation. The critical temperature was found to increase in August, and to reach its maximum in October.

A definite relationship was found to exist between the Hehner value and the critical temperature, and this is expressed by *Crismer* in the following table :—

	Alcohol with 9 per cent. Water.	Absolute Alcohol.	Hehner Value.
	° C.	° C.	
Critical temperature below .	100	54	86-88
,, ,, from .	100-108	54-62	88-90·5
,, ,, ,, .	108-118	62-72	90-93·3
,, ,, ,, .	118-124	72-78	93-95·5

A ratio was established between the Reichert-Meissl value and the critical temperature, the sum of the two figures giving a constant number. With alcohol of specific gravity 0·8195 this was 129, and with absolute alcohol 83·5. Hence the Reichert-Meissl value can be calculated by deducting the critical temperature from these respective constants.

Asboth [1] confirmed Crismer's figures in the main. The greatest

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[1] *Chem. Zeit.*, 1896, xx., 685.

difference found by him between butter and oleo-margarine was 30·5° (*Crismer* 30°), and the smallest 27° (*Crismer* 16°); whilst the greatest and smallest differences between butter and margarine were 23° C. and 18° C.

This method has been applied by *Crismer* and *Motteu* [1] to the determination of the amount of water in butter, the following example illustrating the details. The butter fat gave a critical temperature of 98° C., with 91 per cent. alcohol :—

Amount of butter taken, . .	0·7805 gramme	
Water found by evaporation,. .	0·1245 ,,	= 13·75 per cent.
Alcohol containing 1·344 per cent. water,	1·219 ,,	= 1·5 c.c.
Critical temperature, . . .	106·5° C.	

This temperature corresponds to an alcohol containing 10·5 per cent. of water, whilst the alcohol used contained 1·2028 grammes of alcohol and 0·01638 gramme of water. The proportion 89·5 : 10·5 : : 1·2028 : *x* gives 1·1411 grammes as the amount of water in the alcohol containing 10·5 per cent., of which 0·01638 gramme was originally present. Hence the amount of water derived from the butter was 0·1247 gramme, or 13·77 per cent.

In the case of salted butter the results thus obtained are too high.

Viscosimetrical Examination.—*Killing* [2] has constructed a special apparatus for judging as to the purity of butter from the number of seconds occupied by a definite volume in running out at 40° C. Each apparatus is standardised for the mean efflux time of butter fat and margarine before being sold.

With one apparatus, *Killing* obtained readings of 4 minutes 11·66 seconds to 4 minutes 15 seconds with eleven samples of margarine, the mean being 4 minutes 12·77 seconds; whilst the corresponding limits with eight samples of butter were 3 minutes 42 seconds and 3 minutes 46 seconds, and the mean 3 minutes 43·8 seconds. In the same apparatus, lard gave 4 minutes 26 seconds to 4 minutes 30 seconds, and beef fat 4 minutes 31 seconds to 4 minutes 35·5 seconds.

Wender [3] uses a solution of the fat in chloroform for the determination of the viscosity, and takes the viscosity of the solvent into account. In this way he found samples of butter fat from different sources to require in the mean 20·04 seconds at 20° C. The time taken by chloroform was fixed as 100, and on this basis the viscosity value for pure butter fat averaged 344·30 and for margarine 373·2.

Each increase of 1° in the temperature above 20° C. decreased the efflux time by 1·45 seconds.

Wender found that this method gave as good results as any other physical test in the case of mixtures, but that it was not possible to detect a small proportion of margarine by its means.

Refractometric Examination.—The instruments in general use for determining the refractive power of butter are the oleo-refractometer

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[1] *Bull. de l'Ass. belge Chim.*, 1896, ix., 359.

[2] *Zeit. angew. Chem.*, 1894, 643, 739 ; 1895, 102.

[3] *J. Amer. Chem. Soc.*, 1895, xvii., 719.

of Amagat and Jean, and the butyro-refractometer of Zeiss, either of which may furnish valuable evidence of the presence of foreign fats in the butter (see Chap. IV.).

Oleo-refractometer.—In using this instrument, *Jean*[1] melts the butter at a temperature not exceeding 50° C., stirs the liquid with a little gypsum, and decants the fatty layer through cotton wool. The filtered fat is then examined with Amagat and Jean's apparatus at 45° C.

Jean found that pure butter of different origin gave readings of − 29° to − 31°.

With Dutch butters, readings as low as − 25 have often been obtained, so that the evidence afforded by this instrument cannot be regarded as conclusive.

Ellinger[2] obtained results ranging from − 23° to − 35° with 510 samples of Danish butter, the readings being taken at 45° C.

A similarly wide range was observed by *Pearmain*,[3] whose readings with fifteen samples varied from − 25° to − 34°, the average being − 30°. The greatest difference in the specimens of margarine examined by *Pearmain* was − 13 and − 18.

Butyro-refractometer.—*Wollny* obtained the following results with a large number of samples of butter and margarine :—

	Temperature.	Refractometer Reading.	Refractive Index, n_D.
	° C.		
Butter, . .	25	49·5-54·0	1·4590-1·4620
Margarine, . .	25	58·6-66·4	1·4650-1·4700
Mixtures, . .	25	54·0-64·8	1·4620-1·4690

The values obtained by *Thorpe*[4] in the examination of 371 samples of English butter of various origin ranged from 37·3 to 43·0 at 45° C., whilst Dutch butters have given readings of 42·0 to 47·6.

Delaite[5] shows that, contrary to Zeiss's assertion, the reading obtained at 25° C. differs from that found at a higher temperature and reduced to 25° C. In his opinion, the test cannot be relied upon even as a preliminary one, for although the average butter gives a reading not higher than 44 at 40° C., yet samples of undoubted purity often give higher figures. On the other hand, abnormal and adulterated butter may give readings as low as 41·6. Rancidity also lowers the result so that a strongly rancid adulterated butter may give a lower figure than a genuine sample.

Crismer[6] also points out that in some cases an adulterated sample

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[1] *Chim. anal. des Matières grasses.*

[2] *Analyst*, 1891, xvi., 197.

[3] *Ibid.*, 1895, xx., 135.

[4] *J. Chem. Soc.*, 1904, lxxxv., 257.

[5] *Bull. de l'Ass. belge Chim.*, 1894, vii., 145.

[6] *Bull. de l'Ass. belge Chim.*, 1897, x., 453.

may give lower figures than genuine butter. This is illustrated by a number of examples of which the following are typical :—

	Abbé-Zeiss Refractometer at 40° C.	Insoluble Fatty Acids.	Critical Temperature + Acidity.
Butter, adulterated,	45·2	91·48	66·3
" "	45·6	91·48	67·5
" pure, .	45·8	..	57
" " .	46	..	59·5

Partheil and *Velsen*[1] show, by means of experiments with artificial triglycerides, that the refractive index increases with the rise in the iodine value, but that an increase in the Reichert-Meissl value has but little effect upon the refraction.

Free Fatty Acids.—According to *Duclaux*, the proportion of these in fresh butter varies from 0·005 to 0·010 gramme per kilo. ; but on keeping the quantity gradually increases. It is thus possible to form some idea of the freshness of butter from a determination of the acid value, and the test is recommended by *Cochran* for the identification of renovated butter (*vide infra*).

Saponification Value.—This is very high owing to the amount of acids of lower molecular weight contained in butter.

According to *Brown* (*loc. cit.*) the general limits are 220 to 236, whilst the extreme limits recorded are 216 (*Samelson*) and 245 (*Fischer*).

Since coconut oil and palm-kernel oil have also high saponification values, mixtures of these oils with animal fat can readily be prepared, giving the same results as genuine butter fat.

Brown finds that, as a rule, an increase in the saponification value is accompanied by an increase in the Reichert value and a decrease in the iodine value.

Iodine Value.—This is greatly influenced by the nature of the food given to the cows, and it is not of much use as a means of detecting adulteration.

Brown (*loc. cit.*) gives 26 to 38 as the usual limits, the extreme limits recorded being 19·5 (*Moore*), and 49·57 (*Farnsteiner* and *Karsch*).

Hehner and *Mitchell* have shown that the heat of bromination corresponds with the iodine value, and their method can be relied upon for a rapid determination of the amount of halogen absorbed.

Methods of Examining Butter.

Determination of Water.—A weighed quantity of the butter is dried in a hot-air oven at 110° to 120° C. until constant in weight.

A more rapid method, which gives sufficiently accurate results for practical purposes, is to heat the butter in a porcelain dish over the

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[1] *Chem. Centralbl.*, 1906, ii., 215.

blue flame of an argand burner, stirring it all the time until the first signs of the curd charring, and then to weigh the residue, or by mixing the butter with ignited sand the water may be expelled at a low temperature without loss by spirting, and no attention is required.

Distillation methods have also been introduced.[1]

Determination of Non-Fatty Solids.—The residue from the determination of the water is repeatedly extracted with a suitable solvent, such as ether, chloroform, or petroleum spirit, to remove the fat, and the residue dried and weighed.

Curd or Casein.—The proportion of casein in the solids not fat can be calculated, as suggested by *König*, by determining the amount of nitrogen and multiplying the result by 6·25. In this way *König* found the percentage to vary from 0·19 to 4·78 in 302 samples of butter.

Salts.—These are determined by igniting the residue of non-fatty solids at as low a temperature as possible, and weighing the ash.

Sodium Chloride is determined by titrating a solution of the ash with standard silver nitrate solution, or it may be precipitated from the aqueous layer separated from the butter fat.

Milk-sugar is generally calculated by difference.

Preservatives.—Numerous antiseptic agents have been employed as preservatives in butter, but none so frequently as boric acid or borates, which are widely used at the present day.

Boric acid is readily identified by testing the aqueous layer, which separates on melting the butter, with turmeric paper in the usual manner.

It can be determined by distilling the liquid with methyl alcohol acidified with sulphuric acid, collecting the boric acid distilling over in sodium phosphate solution of known strength, evaporating the liquid to dryness, and weighing the residue (*Hehner*).

Salicylic Acid is occasionally used as a preservative. The method used for its determination in the Paris Public Laboratory is as follows:—About 20 grammes of the butter are repeatedly extracted with a solution of sodium bicarbonate, and the extract, which will contain the salicylic acid in the form of salicylate, acidified with sulphuric acid, and extracted with ether. The residue left on evaporation of the ether is treated with a little mercurous nitrate solution, and the resulting insoluble precipitate washed, and treated with dilute sulphuric acid again to liberate the salicylic acid, which is then redissolved in ether, the solution evaporated, and the residue dried at 80° C. to 100° C. Finally, it is extracted with petroleum spirit to separate it from any other acid that may be present, the extract mixed with an equal quantity of alcohol (95 per cent.), and the liquid titrated with $\frac{N}{10}$ alkali, phenol-phthalein being used as indicator. Each c.c. of the alkali used is equivalent to 0·0138 gramme of salicylic acid.

A colorimetric estimation has been based upon the violet coloration given by salicylic acid with ferric salts, the colour obtained on

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[1] *U.S. Dept. Agric., Bureau of Animal Industry*, Circ., 100.

gradually adding a very dilute solution of ferric chloride being compared with that given by an aqueous solution of a known quantity of the acid.

Formaldehyde is now rarely added to butter. It can be detected by testing the distillate by Hehner's tests.[1]

Glucose.—According to *Cochran*,[2] glucose has been used as a preservative for butter intended for tropical countries, especially by French manufacturers. To detect it, 10 grammes of the butter are repeatedly extracted with boiling water, and the filtered extract tested with Fehling's solution.

Colouring Matters.—The natural colour of butter varies with the season, that churned in the winter being usually much whiter than the summer product. On exposing naturally yellow butter to the influence of light and air it is rapidly bleached.

Artificial colouring matters are frequently added with the object of making the butter appear richer.

For their detection *Moore* [3] recommends shaking 5 grammes of the butter with 25 c.c. of a mixture of methylic alcohol (15 c.c.) and carbon bisulphide (2 c.c.), any colouring matter present being found in the upper alcoholic layer, which separates on standing.

It has been pointed out by *Stebbins*,[4] however, that the colouring matter of the carrot is more soluble in carbon bisulphide than in alcohol, and he, therefore, mixes the melted fat (50 grammes) with about a fifth part of its weight of finely-powdered fuller's earth, and decants the hot fat from the deposit formed on standing. This deposit is then repeatedly washed with benzene (the filtrates being tested for carrotin), then dried on the water-bath, and extracted with three successive portions of 20 c.c. of 94 per cent. alcohol, and the residue left on evaporation of the combined extracts, dried, weighed, and tested for the separate colouring matters.

Leeds [5] has described the following method :—100 grammes of the butter are shaken in a separating funnel with 300 c.c. of petroleum spirit (sp. gr. 0·638), the curd and water drawn off, and the petroleum spirit solution washed with water and allowed to stand for twelve to fifteen hours at 0° C., so as to allow the bulk of the solid glycerides to crystallise. The solvent is then decanted and shaken with 50 c.c. of $\frac{N}{10}$ alkali, which will extract the colouring matters. The aqueous layer is now drawn off and rendered just acid to litmus with hydrochloric acid, the resulting precipitate being washed on a weighed filter with cold water, dried, and weighed.

The nature of the colouring matters present is then determined by dissolving the precipitate in alcohol and testing a few drops of the solution with an equal quantity of the different reagents mentioned in the subjoined table :—

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[1] *Analyst*, 1896, xxi., 96.

[2] *J. Amer. Chem. Soc.*, 1898, xx., 201.

[3] *Analyst*, 1886, xi., 163.

[4] *J. Amer. Chem. Soc.*, 1887, 41.

[5] *Analyst*, 1887, xii., 150.

Colouring Matter.	Concentrated H_2SO_4.	Concentrated HNO_3.	$H_2SO_4 + HNO_3$.	Concentrated HCl.
Annatto, . . .	Indigo blue, then violet.	Blue, then colourless.	Same.	No change, or only slight dirty yellow or brown.
Annatto + decolorised butter,	Blue, changing to green and then to violet.	Blue, then green and bleached.	Decolorised.	No change, or only slight dirty yellow.
Turmeric, . . .	Pure violet.	Violet.	Violet.	Violet, changing to original colour on evaporation of HCl.
Turmeric + decolorised butter,	Violet to purple.	Violet to reddish-violet.	Same.	Fine violet.
Saffron, ...	Violet to cobalt blue, changing to reddish-brown.	Light blue, changing to light reddish-brown.	Same.	Yellow, changing to dirty yellow.
Saffron + decolorised butter,	Dark blue, changing quickly to reddish-brown.	Blue, through green to brown.	Blue, quickly changing to purple.	Yellow, becoming dirty yellow.
Carrotin, . . .	Umber brown.	Decolorised.	Do., with NO_2 fumes and odour of burnt sugar.	No change.
Carrot + decolorised butter,	Reddish-brown to purple, similar to turmeric.	Yellow and decolorised.	Same.	Slightly brown.
Marigold, . . .	Dark olive-green, permanent.	Blue, changing instantly to dirty yellow-green.	Green.	Green to yellowish-green
Safflower. . . .	Light brown.	Partially decolorised.	Decolorised.	No change.
Aniline yellow, . .	Yellow.	Yellow.	Yellow.	Yellow.
Martius yellow, . .	Pale yellow.	Yellow, reddish precipitate, magenta at margin.	Yellow.	Yellow, precipitate treated with NH_3 and ignited deflagrates.
Victoria yellow, . .	Partially decolorised.	Same.	Same.	Same, colour returns on neutralising with NH_3.

Turmeric, which is one of the constituents of a colouring matter for butter used in France, gives a yellowish-brown colour with ammonia and a reddish-brown colour with hydrochloric acid. When present, it may interfere with the sesamé oil test (*vide infra*).

Microscopical Examination.—An examination of the fat with polarised light under the microscope may frequently be of service in detecting the presence of foreign fats, owing to the fact that butter fat does not, as a rule, assume a crystalline structure, as is the case with the fats used in the manufacture of margarine.

On account of this difference in structure most butters appear dark, or practically so, when examined with polarised light. *Richmond*,[1] however, has shown that under certain conditions butter fat may assume a crystalline structure, and present the bright appearance of butter containing margarine. For instance, this is the case with butter prepared from very fresh milk that has not been artificially cooled, or churned on a very hot day, and in butter that has travelled a long distance, and so has been subjected to the influence of vibration. Hence, *Richmond* considers that the results of the test must be accepted with reserve.

Renovated or "Process" Butter.—This is the name given to stale or unsaleable butter that has been melted down and the fat congealed on ice, or churned again with milk and butter-milk, and sold as fresh butter. The coagulated added milk furnishes an artificial curd containing about the same proportion of nitrogen as that of genuine butter. Through this process of melting the fat assumes a distinct crystalline structure, which *Cochran* [2] regards as a reliable means of identification.

When examined under the microscope with polarised light with the selenite plate, and with the analyser in any position, fresh butter fat shows a uniformly coloured field, whilst that of renovated butter is mottled and variegated in colour. Without the selenite plate the field in the case of pure butter is nearly uniformly dark, whilst renovated butter shows white patches.

Cochran never observed these white patches in the case of old genuine butter, which frequently shows the variegated field with the selenite plate (*vide supra*).

A further test recommended by *Cochran* is that the Valenta test shows a lower temperature and that more acetic acid is dissolved by renovated butter, whilst there is usually a high proportion of free fatty acids. The results obtained with samples of renovated butter are shown in the following table :—

	Turbidity Temperature, Valenta Test.	Acetic Acid Dissolved.	N-alkali required to Neutralise 100 gms. of Fat.
	° C.	Per cent.	° C.
Fresh butter, . .	60·0	70	1·1
Renovated butter, . .	48·5	100	6·5
,, ,, . .	50·0	100	9·4
,, ,, . .	49·0	100	8·1

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[1] *British Food Journal*, 1901, iii., 374. [2] *J. Franklin Instit.*, 1899, cxlvii., 85.

Hess and *Doolittle* rely chiefly upon an examination of the curd to detect " process " butter. They state that on heating the sample over a naked flame genuine butter foams, whilst renovated butter splutters and does not foam. Margarine behaves like process butter, but can be identified by other tests. This difference is due to the cohesive properties of the curd of pure butter.

The curds, when separated from the fat and washed with ether, show marked differences. Thus genuine butter curd, the proteid of cream, is a gelatinous amorphous mass, which is only soluble with difficulty in acids and alkalis. The curd from process butter is flaky, granular, and non-cohesive, and dissolves readily in acids or alkalis. It is the proteid of milk (casein).

A further test is furnished by melting the samples, separating the fat, and transferring the aqueous layer to a moistened filter. The filtrate, boiled with a few drops of acetic acid, gives a flocculent precipitate of milk albumins in the case of process butter, whereas in the case of pure butter only a slight milkiness results.

In the case of the curd from milk the ratio of casein to albumins should be the same as in milk (9 : 1). In the " process " butters *Hess* and *Doolittle* [1] found the ratio to be as 8·6 is to 1.

In making this estimation they extracted the fat from 50 grammes of the sample with ether, washed the casein with water, and determined the amount of nitrogen by Kjeldahl's method. The filtrate from the curd was acidified with acetic acid, boiled, the precipitated albumins collected on a filter, and their amount calculated from the amount of nitrogen they contained.

Detection of Foreign Fat in Butter.

The general conclusions drawn from the determination of the physical and chemical characteristics of the fat may be supplemented by certain special tests.

Phytosterol Tests.—As margarine is prepared from animal fats, mixed with vegetable oils or fats, or from vegetable fats alone, the examination of the unsaponifiable matter by Bömer's phytosterol and phytosteryl acetate tests (*q.v.*) affords a reliable means of detecting even a small addition.

Tests for Special Oils.—In addition to this general test for vegetable oils, the special tests for cotton-seed oil, sesamé oil, and earth-nut oil (arachidic acid), which are described under those several oils, should also be made.

Sesamé Oil.—The red coloration given by turmeric with hydrochloric acid may cause uncertainty in the test for sesamé oil. To obviate this *Hanause* [2] adds 5 c.c. of glacial acetic acid to the butter,

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[1] *J. Amer. Chem. Soc.*, 1900, xxii., 150.

[2] *J. Pharm. Chim.*, 1897, vii., 350

and boils the mixture before adding the furfural reagent. In the absence of sesamé oil the acid layer only acquires a faint rose coloration, whereas when that oil is present the colour is reddish-violet, and the fatty layer above is yellowish-rose when hot, and yellowish-white when cold.

According to *Wauters*,[1] butter or margarine can be decolorised with animal charcoal without removing the active constituent of sesamé oil.

Amthor[2] states that unfiltered butter gives a violet coloration when heated with hydrochloric acid alone, but that old butter from which the lactose has disappeared no longer reacts. He attributes this coloration to the action of the furfural produced upon protein substances in the butter.

Influences of the Cow's Food on the Colour Reactions.—Numerous experiments have been made to determine whether feeding the cows with special oil-cake would cause the reaction for the special oil to be given by the butter prepared from the milk.

Werenskiold[3] was unable to detect arachidic acid in the butter of Norwegian cows fed upon 1 kilo. of earth-nut cake per day, though he obtained the reactions for cotton-seed oil with the butter from cows fed upon cotton-seed cake.

Experiments made on behalf of the Board of Agriculture[4] show that cows fed upon cotton-seed cake invariably yield butter showing the reactions for cotton-seed oil, though, as a rule, the intensity of the reaction indicates less than 1 per cent.

No sesamé oil reaction was obtained with the butter from cows fed for two months upon as much sesamé cake as they were willing to eat.

Detection of Coconut Oil.—Since coconut oil contains a considerable proportion of volatile fatty acids, the Reichert value is often inconclusive in the case of butter containing that fat. The tests for its detection are therefore based upon the fact that it contains a large amount of the acids intermediate between the volatile and non-volatile acids (myristic, etc.). The solubility tests and extended Reichert value are described under *Coconut oil.*

Reychler's[5] method of applying the latter test is based upon the ratio of the total volatile fatty acids and soluble volatile fatty acids. Instead of filtering the distillate, he adds 50 c.c. of alcohol, and, if necessary, a little ether, and thus obtains a measure of the insoluble fatty acids simultaneously distilled.

The following results illustrate this method :—

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[1] *Bull. de l'Ass. belge Chim.*, 1899, xiii., 404.

[2] *Zeit. Untersuch. Nahr. Genussm.*, 1900, iii., 233.

[3] *Chem Centralbl.*, 1900, ii., 215.

[4] *Analyst*, 1898, xxiii., 255.

[5] *Bull. Soc. Chim.*, 1901, xxv., 142.

	I. Total Volatile Acids.	II. Soluble Volatile Acids.	Ratio of II. and I.
1. Butter, ...	32·4	29·36	0·91
2. Coconut oil, ...	22·7	7·4	0·33
3. Mixture : 79·4 per cent. butter, . 20·6 ,, ,, coconut oil,	31·4	24·4	0·78
4. Butter, ...	32·0	28·6	0·89
5. Coconut oil, ...	22·2	7·2	0·32
6. Mixture I. : 75 per cent. oleo-margarine, 25 ,, ,, lard, . .	1·50	0·83	0·55
7. ,, II. : 50 per cent. of Mixture I., 50 ,, ,, ,, coconut oil,	12·45	5·6	0·45
8. ,, III : 19·75 per cent. of Mixture II., 80·25 ,, ,, ,, butter,	28·6	24·3	0·85

Coconut and Palm-kernel Oil in Butter.

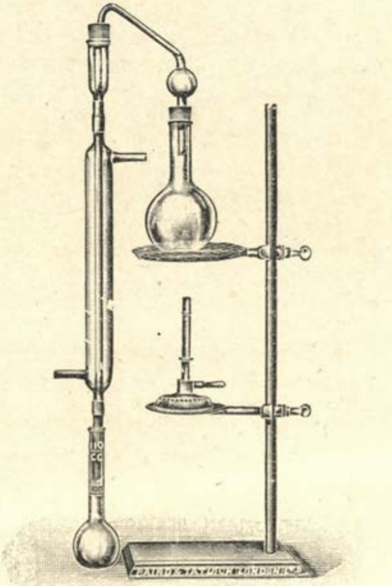

Fig. 104.—Polenske's Standard Apparatus.

The Polenske Value.—The proportion of volatile insoluble fatty acids obtained under specified conditions affords an indication of the presence of coconut oil (see p. 244).

The standard method of determining this value is as follows:—Five grms. of the filtered butter fat are heated over a free flame in a 300 c.c. flask with 20 c.c. of glycerin and 2 c.c. of an aqueous solution (1 : 1) of sodium hydroxide. The soap solution is allowed to cool below 100° C. diluted with 90 c.c. of water, and heated on the water-bath at about 50° C. until the soap dissolves. The hot soap solution, which must be clear and practically colourless, is treated with 50 c.c. of dilute sulphuric acid (25 c.c. H_2SO_4 per litre), and a few fragments of pumice, and the flask is connected with the condenser as shown in Fig. 104. It is essential that each part of this apparatus should be of the exact dimensions indicated in the original paper.[1]

The flask is heated in such a way that from 19 to 20 minutes are required for the distillation of 110 c.c., and the temperature of the distillate falling into the flask must not exceed 20° to 23° C.

After 110 c.c. have been collected the flask is replaced by a 20 c.c. graduated cylinder, and, without shaking, is immersed, nearly to the top, in water at 15° C. After about five minutes any oily drops adhering to the surface of the liquid are made to adhere to the sides of the flask by gently tapping the neck, and the flask is left for a further ten minutes in water. It is then closed with a cork and gently inverted several times, so as to effect thorough admixture of its contents, a note being taken of the character of the insoluble fatty acids (*i.e.*, whether semi-solid or oily).

Of this distillate, 100 c.c. are filtered through a paper 8 cm. in diameter, and the filtrate is titrated with $\frac{N}{10}$ potassium hydroxide solution, as in the ordinary method of determining the Reichert-Meissl value.

The insoluble volatile acids on the filter are washed with three successive portions of 15 c.c. of water, each of which has been passed through the condenser tube, the cylinder, and the flask, and the washings containing the soluble volatile acids are rejected.

The insoluble volatile acids adhering to the inside of the condenser tube, the sides of the cylinder, and the walls of the flask, are removed by three successive washings (15 c.c. each time) of neutralised 90 per cent. alcohol. These washings are poured over the filter, each being left to drain before the next is added, and the alcoholic filtrate is titrated with $\frac{N}{10}$ alkali solution.

Blichfeldt's Method.—To obviate the risk of losing some of the fatty acids while washing them out of the cylinder with alcohol, *Blichfeldt*[2] has devised a form of apparatus in which the distillation flask is connected with the side tube of an inverted vertical condenser, upon the base of which two bulbs are blown. After the distillation, the bulbs are washed out with standard sodium hydroxide solution, and the excess of alkali titrated with standard acid.

A measured quantity of silver nitrate solution is then added to precipitate the insoluble silver salts of the insoluble fatty acids, a little sodium nitrate being used to accelerate the precipitation. The liquid is made up to a definite volume and filtered, and the excess of silver in an aliquot part of the filtrate is titrated with standard sodium chloride solution. The difference between the equivalent of the total volatile acids and the equivalent of the acids yielding insoluble silver salts, gives the equivalent of the soluble silver salts.

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[1] *Analyst*, 1904, xxix., 154.

[2] *J. Soc. Chem. Ind.*, 1910, xxix., 792.

Typical results obtained by this method were as follows:—

	Total Volatile Fatty Acids.	Soluble Silver Salts.	Insoluble Silver Salts.
Butter,	32	29	3
Coconut oil,	20	14	16
Palm-kernel oil,	15	3	12

Shrewsbury and Knapp's Method.—This method is based upon the fact that lauric acid, which is the predominating fatty acid in coconut oil, is readily soluble in dilute alcohol, and may be determined by titrating the solution with standard alkali.

The alcohol consists of methylated spirit of specific gravity 0·822 and 36 c.c. of water at 15° to 17° C.[1]

The following results were obtained by titrating 70 c.c. of the alcoholic filtrate with $\frac{N}{10}$ sodium hydroxide in the case of pure triglycerides:—Tributyrin, 0; trilaurin, 176; trimyristin, 51; tripalmitin, 16; tristearin, 6; and triolein, 65 c.c.

Coconut oil gave a value of 163, whilst 14 samples of pure butter fat gave results ranging from 23·6 to 31·2, with an average of 27·7. The fat from cream gave a value of 30, and lard a value of 15·7, whilst a mixture of butter (average value 25) with 5 per cent. of coconut oil gave a value of 33, and with 15 per cent. a value of 38·0 c.c.

It was found that the proportion of coconut oil calculated from the results of this method were about 5 per cent. too high.

The method may also be used for detecting coconut oil in margarine, in which the Reichert-Meissl value suggests the presence of more than the permissible 10 per cent. of butter (see p. 644).

Turbidity Temperature of Barium Salts.—A method for the detection and approximate estimation of coconut and palm-kernel oils in butter has been based by *Burnett* and *Revis*[2] upon the degree of solubility in alcohol of the barium salts of the insoluble fatty acids.

The Polenske value is determined by the method described (*supra*), with the exception that $\frac{N}{10}$ baryta solution is used for the titration.

The insoluble barium salts are washed with alcohol of 93 per cent. strength (sp. gr. 0·8235 at 15° C.), and dissolved in boiling alcohol (10 times the quantity in c.c. of the Polenske value), the flask being heated beneath a reflux condenser.

The solution is stirred in a closed test-tube, and the temperature at which it becomes turbid is noted.

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[1] *Analyst*, 1910, xxxv., 385.

[2] *Analyst*, 1913, xxxviii., 255.

It was found that coconut oil gave a turbidity temperature of 52·5° C., and palm-kernel oil of 58·5° C., whilst mixtures of the two fats gave results corresponding with their respective proportions. Palm-kernel "oleine" and "stearine" became turbid at 59·5° and 72·5° C. respectively, and cohune oil behaved like coconut oil.

The drawback of this method is that slight variations in the strength of the alcohol will affect the turbidity temperatures.

Butter of Other Animals.—The butter obtained from the milk of other terrestrial animals closely resembles cow's butter in character.

Schmidt[1] gives the following comparative figures obtained with the butter fat from ewe's milk and goat's milk, and to these may be appended the figures found by *Strohmer*[1] for buffalo's butter and cow's butter :—

Butter from	Melting Point.	Volatile Acids as Butyric.	Insoluble Fatty Acids.	Melting Point of Fatty Acids.
	° C.	Per cent.	Per cent.	° C.
Goat's milk, . .	33·5	4·50	84·40	38·8
Ewe's milk, . .	37·5	4·77	85·25	40·5

Butter from	Melting Point.	Solidification Point.	Solidification Point of Fatty Acids.	Saponification Value.	Reichert-Meissl Value.
	° C.	° C.	° C.		
Buffalo's milk .	31·3	19·8	37·9	222·4	30·4
Cow's milk, .	31·0-31·5	19-20	37·5-38	227·0	21·5-32·0

The proximate percentage composition of buffalo and goat's butter was found by *Fleischmann* and *Strohmer*, and by *Schmid* to be as follows :—

Butter from	Water.	Fat.	Casein.	Milk Sugar.	Salts.
Buffalo's milk, .	16·59	81·64	1·60		0·17
Goat's milk, . .	22·40	75·0	1·75	0·67	0·18

Allen[2] found a specimen of porpoise butter to contain 4·57 per cent. of volatile acids expressed as valeric acid, which was the chief volatile fatty acid present.

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[1] König, *Chem. menschl. Nahr. Genussm.*, ii., 303.

[2] *Commercial Organic Analysis*, ii., [i.], 180.

DEER FAT.

Recorded Values.

Deer Fat.

Fat from	Specific Gravity.	Saponification Value.		Iodine Value.		Melting Point.		Solidification Point. Fatty Acids.	Hehner Value.	Reichert Value.	Authority.
		Fat.	Fatty Acids.	Fat.	Fatty Acids.	Fat.	Fatty Acids.				
						° C.	° C.	° C.			
Stag, .	0·9670	199·9	201·3	25·7	23·6	51-52	50-52	46-48	...	·66	Amthor & Zink.[1]
Elk, .	0·9625	195·1	201·4	35·0	27·8	49-52	53-55	48-50	...	0·78	,,
,, .	...	...	200	35·9	...	...	...	46·7	...	...	Shukoff.[2]
Fallow deer,	0·9615	195·6	201·4	26·4	28·2	52-53	50-53	47-48	...	1·70	Amthor & Zink
Roebuck,	0·9659	199·0	200·5	32·1	27·9	52-54	62-64	49-50	95·8	0·68	,,
Reindeer,	...	194·4-198·8	...	31·4-35·8	34·5	47·8	...	45·7	...	...	Rarassew.[3]

The fat obtained from different species of deer is hard and white, and closely resembles beef tallow in its general characteristics.

Elk tallow, according to *Shukoff*, contains 0·52 per cent. of water, 1·8 per cent. of free fatty acids, and 0·23 per cent. of unsaponifiable matter.

The acid values of the other fats given above were as follows :—Elk, 0·87; stag, 3·50; fallow deer, 2·90; roebuck, 1·74; and reindeer, 4·35 to 5·3.

Reindeer tallow is chiefly used locally for food and dip candles, and does not often come into the market. A specimen examined by *Rarassew* contained 10·4 per cent. of glycerol, 61·1 per cent. of stearic acid, 1·4 per cent. of palmitic acid, and 38·5 per cent. of oleic acid.

GOOSE FAT.

Recorded Values.

Goose Fat.

Origin.	Specific Gravity at 15° C.	Saponification Value.	Hehner Value.	Reichert Value.	Iodine Value.	Melting Point.	Refractometer (*Zeiss*) at 40° C.	Authority.
						° C.		
From 4 parts of the same bird,	0·9228 to 0·9300	191·2 to 193·0	94·5 to 95·3	0·2 to 0·3	58·7 to 66·4	27·5 to 31·7	50·0 to 50·5	Rozsenyi.[4]
Tame goose, .	0·9274	193·1	...	0·98	67·6	32-34	...	Amthor & Zink [5]
Wild goose, .	...	...	...	...	99·6	...	...	,,
Wild goose, 2 years in captivity,	0·9158	196·0	...	...	67·0	...	...	,,

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[1] *Zeit. anal. Chem.*, 1897, xxxvi., 1.

[2] *Chem. Rev. Fett Ind.*, 1901, viii., 229.

[3] *Ibid.*, 1902, ix., 58.

[4] *Analyst*, 1896, xxi., 235.

[5] *Zeit. anal. Chem.*, 1897, xxxvi., 1.

Fatty Acids.

Origin.	Melting Point.	Solidification Point.	Iodine Value.	Specific Gravity at 15° C.	Authority.
	° C.	° C.			
From 4 parts of the same bird,	36·6-40·2	...	...	...	Rozsenyi.
Tame goose, . .	38-40	31-32	65·3	0·9257	Amthor and Zink.
Wild goose, . .	34-40	33-34	...	...	,,
Wild goose, 2 years in captivity,	36-38	32	65·1	0·9251	,,

Goose fat, as obtained from the domestic fowl, is a pale yellow, soft, semi-solid mass, but that of the wild goose is an oil with a much higher iodine value. It is noteworthy that the fat of a wild goose kept in captivity for two years was found by *Amthor* and *Zink* to have practically the same iodine value as the fat of a tame goose.

Polenske's[1] method (p. 679) is applicable to the detection of goose fat in some other fats.

HEN'S EGG OIL.

Recorded Values.

Hen's Egg Oil.

Specific Gravity.	Acid Value.	Saponification Value.	Reichert-Meissl Value.	Iodine Value.	Hehner Value.	Melting Point.	Solidification Point.	Authority.
° C.						° C.	° C.	
0·9156 at 20°	...	185·2 to 186·7	...	81·2 to 81·6	...	22 to 22·5	8 to 10	Paladino & Toso (*a*).
0·9144 at 15°	1·2	190·2	0·4	72·1	95·16	...	...	Kitt (*b*).

(*a*) Expressed oil. (*b*) Oil extracted with ether.

Fatty Acids.

Melting Point.	Saponification Value.	Mean Molecular Equivalent.	Iodine Value.	Acetyl Value.	Authority.
° C.					
34·5-35	...	...	...	...	Paladino and Toso.
36-39	194·9	285·0	73·7	11·9	Kitt.

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[1] *Arbeit. Kaiserl. Gesund. Amt.*, 1907, xxvi., 444.

The yolk of a hen's egg contains from 25 to 30 per cent. of oil, which can be extracted or expressed from the dried substance. The expressed oil is a clear yellow limpid fluid which becomes viscous on cooling and yields a crystalline deposit. It readily becomes rancid, and loses its colour on exposure to light and air.

Oil extracted by solvents is semi-solid and of an orange-yellow colour.

The egg oil prepared by *Kitt*[1] contained 10·4 per cent. of glycerol, 0·2 per cent. of lecithin, and 1·5 per cent. of cholesterol. The fatty acids consisted of:—Oleic acid, 81·8 per cent.; palmitic acid, 9·6 per cent.; hydroxystearic acid (?), 6·4 per cent.; and stearic acid, 0·6 per cent.

Paladino and *Toso*[2] found that the melting point of the oil was frequently incomplete, owing to the presence of crystals (probably cholesterol) melting at 145° C.

Egg oil yields a solid elaidin.

HORSE FAT.

Recorded Values.

Horse Fat.

Origin.	Specific Gravity.	Hehner Value.	Saponification Value.	Iodine Value.	Melting Point.	Refractive Index at 60° C.	Authority.
Fat from kidneys,	At 15° C. 0·9320	95·4	198·7	81·09	° C. 39	...	Amthor & Zink.
,, neck, .	0·9330	95·42	199·5	74·84	34-35	...	,,
,, back .	0·9319	94·78	197·8	81·6	36-37	...	,,
,, ,, .	At 17·5°C. 0·9159	...	...	79·9	...	...	Frühling.[3]
,, heart, .	0·9167	...	...	77·4	...	...	,,
,, kidneys,	0·9212	...	...	82·6	...	...	,,
Average, . .	0·9180	...	...	80·0	...	...	,,
Fat from kidneys,	...	...	195·7	85·4	18	...	Hehner & Mitchell.
....	At 15° C. 0·9189	96 to 97·8	195·1 to 196·8	86·1	41·8-43·2	...	Kalmann.
Intermuscular fat,	...	...	...	75·8	...	...	Bremer.
...	At 60° C. 0·894	...	...	...	...	1·455	Procter.
Marrow fat,	0·9204 to 0·9221	...	197 to 200	77·6 to 80·6	29 to 35	...	Zink.

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[1] *Chem. Zeit.*, 1877, xxi., 303.

[2] *J. de Pharm. Chim.*, 1896, xvi., 247.

[3] *Zeit. angew. Chem.*, 1896, 352.

Fatty Acids.

Origin.	Melting Point.	Solidification Point.	Iodine Value.	Iodine Value of Liquid Acids.	Authority.
	° C.	° C.			
Fat from kidneys,	36-37	30-30·5	83-88	...	Amthor and Zink.
„ neck, .	32-33	32-33	74·41	...	„
„ leaf, .	31-32·5	31-32·5	83·37	...	„
„ back, .	52 53	43-45	81·4	...	Frühling.
„ heart, .	40-41	32-34	78 3	...	„
„ kidneys,	53-54	47-48	84·0	...	„
Average, . .	48·8	41·5	81·6	...	„
Fat from kidneys,	37·2	...	...	...	Hehner & Mitchell.
Intermuscular fat,	...	...	...	108·1	Bremer.
...	37·5-39·5	37·3-37·7	-3·9-87·1	...	Kalmann.
Marrow fat, .	42-44	34-36	71·8-72·2	...	Zink.

Horse fat varies in colour from light to dark yellow, and has a consistency similar to that of butter. On standing for some time it yields a small deposit of "stearine."

One specimen of the fat examined by *Hehner* and *Mitchell* contained no stearic acid, though traces of that acid were found in another sample.

Farnsteiner separated 9·9 per cent. of linolic acid in the form of its tetrabromide, but was unable to detect linolenic acid, a conclusion in agreement with the results obtained in the previous experiments of *Hehner* and *Mitchell*.

Horse fat is probably used occasionally as an adulterant of lard, and if only added in small proportion, the addition would not be readily detected.

HUMAN FAT.

Recorded Values.

Human Fat.

Specific Gravity at $\frac{25° C.}{25° C.}$	Acid Value.	Saponification Value.	Reichert Value.	Iodine Value.	Bromine Thermal Value.	Melting Point.	Solidification Point.	Authority.
						° C.	° C.	
0·9033	6·3	195	0·3	61·5	11·3 [= 62·15 I. Value.]	17·5	15	Mitchell.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Iodine Value of Liquid Acids.	Authority.
° C.	° C.			
35·5	30·5	64	92·1	Mitchell.

Chevreul[1] found human fat to consist of an olein and "stearin," the latter being distinguished from mutton stearin in yielding "margaric," and not stearic acid.

Heintz[2] concluded that there were several other acids present besides oleic and palmitic acid.

The specimen of fat examined by the present writer[3] (*M.*) was derived from the kidneys. It was of a pale yellow colour, and had a consistency slightly less than that of butter.

On crystallisation from ether, it yielded a slight deposit (m.p. 51·5° C.), which, under the microscope, showed the crystalline form of the deposit sometimes obtained from flare lards, the crystals having chisel-shaped ends, but being arranged in fan-shaped bunches.

The fatty acids obtained from the lead salts insoluble in ether melted at 35·5° C., and had a molecular equivalent of 278. By crystallisation from alcohol (70 per cent.) crystals melting at 50·5° C. were obtained, whilst the filtrate, on standing, gave a further deposit of crystals melting at the same temperature. Probably myristic acid was one of the fatty acids in these crystals.

LARD.

Recorded Values.

Lard.

Origin.	Specific Gravity.	Hehner Value.	Saponification Value.	Iodine Value.	Refractive Index.	Melting Point.	Solidification Point.	Authority.
	° C.				At 60°C.	° C.	° C.	
Commercial,	0·8985 at $\frac{40^\circ}{15 \cdot 5^\circ}$	...	...	...	...	...	...	Allen.
,,	0·8608 at $\frac{99^\circ}{15 \cdot 5^\circ}$							
,,	0·934-0·938 at 15°	...	...	49·9 to 63·8	...	36 to 45·5	...	Dieterich.
American,	0·890 at 40° 0·860 at 100°	93 to 95	195 to 203	60·3 to 66·5	...	29·8 to 43·9	...	Wiley.
...	...	...	...	...	1·4539	...	...	Thoerner.
American (steam-rendered intestine fat),	0·8595 at $\frac{90^\circ}{15^\circ}$	...	...	47·7 to 58·6	...	...	...	Tennille.
...	0·886 at 60°	...	...	...	1·452	...	...	Procter.
...	...	...	...	...	...	...	27·1-29·9	Goske
Wild boar,	0·9424 at 15°	...	195·1	76·6	...	40-44	...	Amthor and Zink.

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[1] *Recherches sur les Corps Gras.*, 1823.

[2] *Pogg. Anal.*, 1851, 238.

[3] *Analyst*, 1896, xxi., 172.

Fatty Acids.

Origin.	Specific Gravity at $\frac{99^\circ \text{ C.}}{15{\cdot}5^\circ \text{ C.}}$	Melting Point.	Solidification Point.	Iodine Value.	Mean Molecular Equivalent.	Saponification Value.	Authority.
...	0·8445	° C. 44	° C. 39	...	278	201·4	Allen.
Commercial,	...		...	57·5-65·6	...	...	Hehner and Mitchell.
American,	...	36·9-46·6	32·1-42·7	...	...	...	Wiley.
,,	...	...	Dalican's Test. 40·2-42·4	...	...	...	Tennille.
Commercial,	...	...	36-40	60-69·3	...	...	Hehner and Mitchell.
German,	...	...	...	Liquid Acids. 94-96·2	..	...	von Raumer.
American,	...	...	...	104	...	...	,,
Wild boar,	...	39-40	32·5-33·5	81·2	...	...	Amthor and Zink.

Source.—Lard is obtained from the adipose tissue of different parts of the pig. The methods of rendering and the qualities are described in Chaps. X. and XIII.

Composition.—Lard consists mainly of glycerides of palmitic, stearic, and oleic acids, with, at any rate in some cases, small quantities of linolic acid.

By repeated crystallisation of lard from ether *Bömer* was unable to separate any tristearin, whereas that glyceride could be separated from beef and mutton fats. The most insoluble glyceride isolated from lard was about 3 per cent. of a palmito-distearin, which differed in its melting points (68·5° and 51·5° C.), and its crystalline form from the palmito-distearin of mutton fat. About 2 per cent. of stearo-dipalmitin was also separated from lard. The difference in the crystalline form of the distinctive glycerides explains the differences observed in the crystals obtained from lard and beef or mutton fat (p. 680).[1]

Not improbably the more fluid fat from the ham and breast of the pig contains more linolic acid than does the more solid fat, such as that from the flare. If so, this would partly account for the higher iodine value of certain American lards, in which the fat is often of a much more mixed character than in the case of European lards, which are mainly prepared from the fat from the kidneys and bowels.

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[1] *Zeit. Untersuch. Nahr. Genussm.*, 1913, xxv., 321.

Farnsteiner[1] has found not only linolic acid, but also traces of linolenic acid in lard.

Hehner and *Mitchell*[2] examined the fat from different parts of the same pig, and came to the conclusion that the chief fluctuation was in the amount of liquid fatty acids. Assuming the iodine value to represent only oleic acid, and determining the stearic acid by their crystallisation method, they obtained the following approximate results :—

Fat of Somersetshire Pig, 6 months old.	Oleic Acid.	Stearic Acid.	Palmitic Acid.
From	Per cent.	Per cent.	Per cent.
Head, . . .	75	9	16
Ham, . . .	68·5	8·8	22·7
Breast, . . .	71	11·5	17·5
Flare, . . .	58·5	15	26·5
Back, . . .	75	8·8	15·2

The amounts of stearic acid in the saturated fatty acids calculated on this basis were :—Head, 35 ; ham, 28 ; breast, 39·5 ; flare, 36·5 ; and back, 36 per cent.

Stearic Acid in Lards.—*Hehner* and *Mitchell* (*loc. cit.*) found the stearic acid in the mixed fatty acids from lard to vary from 6 to 16 per cent. The following table shows some of their results, with the corresponding iodine values :—

Iodine values, . . .	61·2	57·5	61·2	65·6	63·6
Stearic acid, per cent., .	13·0	16·0	6·7	9·9-10·6	7·4

Water.—As a general rule, lard only contains a small proportion of moisture. *Wiley* found the amount to vary from a trace to 0·7 per cent. in different samples of American manufacture.

Free Fatty Acids.—The amount in fresh lard seldom exceeds 0·5 to 0·8 per cent., expressed in terms of oleic acid.

Variations in Fat from the Same Pig.—The following table gives the analytical values obtained by different chemists with fat from different parts of the same animal :—

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[1] *Zeit. Untersuch. Nahr. Genussm.*, 1899, ii., 1.

[2] *Analyst*, 1896, xxi., 326.

Variations in Analytical Values of Fat from the Same Pig.

Pig's Fat.	Specific Gravity. (At 100° C. Water at 15°=1.)	Melting Point.		Iodine Value.		Authority.
		Fat.	Fatty Acids.	Fat.	Fatty Acids.	
European pigs (mean of 8 results)—		° C.	° C.			
Fat from back, .	0·8607	33·8	40	60·58	61·90	Spaeth.
,, kidney, .	0·8590	43·2	43·2	52·60	54·20	,,
,, leaf, . .	0·8588	44·5	42·9	53·10	54·40	,,
Somersetshire pig, 6 months old—						
Fat from head, .	...	...	34·8	...	67·7	Hehner and Mitchell.[1]
,, ham, .	...	...	34·6	...	61·6	,,
,, breast, .	...	...	36·8	...	64·2	,,
,, flare, .	...	...	40·0	...	52·8	,,
,, back, .	...	...	35·6	...	67·9	,,
American pig—						
Fat from foot, . .	...	35·1	...	77·8	...	Wiley.[2]
,, intestine, .	...	44	...	57·34	...	,,
,, head, .	...	35·5	...	85·0	...	,,
,, kidney, .	...	42·5	...	52·5	...	,,
American pigs—						
Fat from neck, .	...	...	...	65-66·6	...	Voigtländer.[3]
,, back, .	...	...	...	61·5-65·1	...	,,
,, paunch, .	...	...	...	59·0-63·0	...	,,
,, leg, . .	...	...	...	68·8	...	,,
,, ham. . .	...	...	...	66·6 68·4	...	,,
Mixture in equal proportions,	...	...	...	65·5	...	,,

Melting and Solidification Points.—These vary greatly according to the part of the animal whence the fat was derived (*vide supra*).

Goske[4] determines the solidification point in the same manner as Dalican's method for fatty acids. He gives the following results thus obtained :—

Lard.	Solidification Point.
	° C.
Home-rendered lard (3), . . .	26·64-29·95
Pure steam lard (5), . . .	23·6 -27
Lard adulterated with stearine, .	29·7 -36·5

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[1] *Analyst*, 1896, xxi., 326.

[2] *U.S. Dept. Agriculture Bull.*, 13 (1889).

[3] *Zeit. angew. Chem.*, 1898, 857.

[4] *J. Soc. Chem. Ind.*, 1893, xii., 470.

Melting and Solidification Points of Fatty Acids.—These also vary with the origin of the fat, as is shown by *Hehner* and *Mitchell's* results in the table given above.

The following table gives the results of some unpublished experiments made by *Hehner* and *Mitchell* to determine whether any ratio could be found between the iodine values and the solidification points of lard fatty acids :—

		Iodine Value of Fatty Acids.	Solidification Point.
			°C. Dalican's Test.
I.	Lard, ...	63·89	36
II.	,, ...	60	38·5
III.	,, ...	60	40
IV.	,, ...	69·3	37·5
,,	,, + beef stearin, 5 per cent.,	65·9	39·5
,,	,, ,, 10 ,,	62·5	41·0
,,	,, ,, 20 ,,	55·8	43·5

If the liquid fatty acids in lard consisted of only oleic acid, it would doubtless be possible to establish some degree of relationship between the two values, but since more unsaturated fatty acids are also present in varying quantities, the iodine value indicates fatty acids with different influence upon the melting point in different cases.

Iodine Value.—There is a marked difference between the lards of European and American origin as regards their iodine absorption, as will be seen by reference to the tables given above. Hence, before the iodine value can be regarded as an indication of the presence of vegetable oils there must be confirmation from other tests.

Voigtländer (*loc. cit.*) examined 100 samples of American lard, of which 88·5 per cent. had an iodine value of 61 to 66, and 41 per cent. a value above 64.

On the other hand, *Dieterich* found that of 112 samples of German lard 71·7 per cent. had iodine values of 48 to 53, whilst only 2 per cent. gave as high a figure as 64.

Voigtländer deprecates the fixing of any standard for this value, since, in his experience, beef stearine was very frequently found in lards sold in Bavaria, where 62 was at one time adopted as the highest limit for the iodine value.

The iodine value of the wild boar's fat is considerably higher than that of American lard (see *Table of Values*).

Iodine Value of Liquid Fatty Acids.—The determination of the iodine value of the more liquid fatty acids separated by treatment of the lead salts with ether, as first proposed by *Muter* and *de Koningh*, affords much more evidence of the presence of vegetable oils, since a concentration of the more unsaturated fatty acids is thus effected.

This is illustrated by the following results obtained by *Wallenstein* and *Fink*[1]:—

Fat.	Iodine Value of Glycerides.	Iodine Value of Liquid Fatty Acids.
Berlin ox tallow,	38·3	92·2
Australian ,,	45·2	92·4
Hungarian mutton tallow,	38·6	92·7
American "steam lard,"	65·4	104·5
Berlin lard,	52·7	96·6
Hungarian pig's fat,	60·4	96·2
Viennese ,,	60·9	95·2
Roumanian ,,	59·5	96·0
White American cotton-seed oil,	108·0	147·5
Yellow ,, ,, ,,	107·8	147·3
White English ,, ,,	106·5	146·8
Yellow Egyptian ,, ,,	108·0	148·2
White German (bleached) cotton-seed oil,	107·7	147·1
Yellow Peruvian cotton-seed oil,	106·8	147·8
Rape oil,	101·1	120·7
Earth-nut oil,	98·9	128·5
Niger-seed oil,	133·5	147·5
Maize oil,	122·0	140·7
Coconut oil,	8·4	54·0

Lane[2] gives a similar series of iodine values of the liquid fatty acids separated by boiling the lead salts with ether under a reflux condenser, and allowing the liquid to cool slowly :—

Oil or Fat.	Iodine Value of Liquid Acids.
Commercial lard,	95·94
Steam lard,	97·18
Coconut oil,	18·58
Oleo-stearine,	77·82
Cotton-seed oil,	137·3-149·8
Sesamé oil,	139·9
Earth-nut oil,	111-119·5
,, (Chinese),	131
Olive oil,	97·20

See also the results obtained by *Muter* and *de Koningh* (*loc. cit.*).

Bromine Thermal Value.—*Hehner* and *Mitchell*[3] have shown that the rise of temperature on brominating lard corresponds closely

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[1] *Chem. Zeit.*, 1895, xviii., 1189.

[2] *J. Soc. Chem. Ind.*, 1901, xx., 1083.

[3] *Analyst*, 1895, xx., 149.

with the iodine value. Their further experience with lards of all kinds has confirmed the value of this method as a rapid preliminary test.

The following results show the degree of accuracy that can be obtained by this test :—

	Rise of Temperature.	Iodine Value (*Hübl*).	Iodine Value Calculated from Thermal Value.
	° C.		
Lard, ...	10·6	57·15	58·3
,, ...	10·4	57·13	57·2
,, ...	11·2	63·11	61·6
,, ...	11·2	61·49	61·6
,, ...	11·8	64·69	64·9
,, ...	11·8	63·96	64·9
,, ...	10·2	57·15	56·1
,, ...	10·4	57·8	57·2
,, ...	9·0	50·38	49·5
,, ...	11·0	58·84	60·5
,, + 10 per cent. cotton-seed oil,	11·6	64·13	63·8
,, fatty acids, ...	10·4	59·6	57·2
,, ,, ...	11·0	59·15	60·5

Bromine Value.—The results given by M'Ilhiney's method agree well with the iodine value determined by Hübl's method, as is shown by the following figures obtained by *Vulté* and *Logan*.[1]

Iodine Value (*Hübl*).	Iodine Value Calculated from Bromine Value.
76·79-77·36	76·03-75·88

Maumené Test.—As the rise of temperature on treating lard with sulphuric is not great, it is mainly due to the saturation of the unsaturated glycerides, secondary reactions caused by the higher temperatures not occurring as in the case of linseed and other highly unsaturated oils.

Hence the Maumené test in this case corresponds approximately with the iodine value, and, by applying the test in the method described by *Mitchell* (see *Maumené Test*), the correspondence between the two figures is made much closer.

The following table of results obtained by *Tennille*[2] shows the

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[1] *J. Amer. Chem. Soc.*, 1901, xxiii., 156

[2] *Ibid.*, 1895, xvii., 33.

relationship between the iodine values and Maumené figures (obtained by the older method) of a number of different lards :—

	Iodine Value (*Hübl*).	Maumené Test.	Calculated Iodine Value, Maumené Figures, Multiplied by 1·748.
		° C.	
Lard, ...	54·5	30·5	53·31
,, ...	55·6	31·8	55·59
,, ...	58·6	34·8	60·73
,, ...	53·7	30·0	52·44
,, ...	55·4	31·5	55·06
,, ...	56·1	31·7	55·41
,, ...	47·7	25·5	44·57
,, ...	51·7	31·5	55·06
,, ...	52·0	29·5	51·57

Heat of Combustion.—*Schweinitz* and *Emery*[1] consider that this may be of service when considered in conjunction with the iodine value. They give the following results obtained with lards of different origin obtained from Armour & Co. :—

	Melting Point.	Iodine Value.	Combustion. Calories per Gramme.
	° C.		
Lard, leaf, ...	...	56·85	9621
,, caul fat, ...	40·0	58·61	9573
,, intestine fat, . . .	40·7	54·74	9581
,, head fat, ...	29·5	68·79	9503
,, trimmings, ...	...	65·57	9606
,, mixture of all fat, . .	...	63·86	9654
,, compound, 1st grade, .	...	86·18	9583
,, ,, 2nd ,, .	...	86·57	9530
,, shield, ...	...	61·01	9598
,, special pure, . . .	37·5	63·63	9617

The following figures were obtained by *Sherman* and *Snell*[2] with a lard evidently containing a considerable proportion of vegetable oil :—

Specific Gravity at 15° C.	Iodine Value.	Free Fatty Acids as Oleic Acid.	Heat of Combustion. Calories per Gramme.	
			Constant Volume.	Constant Pressure
0·917	74·3	0·74	9451	9466

[1] *J. Amer. Chem. Soc.*, 1896, xviii., 174.

[2] *Ibid.*, 1901, xxiii.

Sulphur Chloride Reaction.—Lard resembles other animal fats in yielding an additional product completely soluble in carbon bisulphide, whilst cotton-seed oil and mixtures of that oil with lard yield hard masses only partially soluble (*Warren*).

Lewkowitsch[1] has found this test of great service in the detection of cotton-seed oil. He gives the following table of results obtained by heating a solution of 5 grammes of the fat in 2 c.c. of carbon bisulphide with 2 c.c. of sulphur chloride :—

Lard.	Cotton-seed Oil.		Solubility of Product in Carbon Bisulphide.
Per cent.	Per cent.		
100	0	No reaction.	Completely soluble.
90	10	Thickens after 35 minutes.	,, ,,
80	20	,, 30 ,,	52 per cent.
70	30	,, 26 ,,	39·6 ,,
60	40	,, 18 ,,	34·8 ,,
50	50	Solid after 10 ,,	37·4 ,,
40	60	,, 8 ,,	30·6 ,,
30	70	,, 7 ,,	32·6 ,,
20	80	,, 6 ,,	30·0 ,,
10	90	,, 4 ,,	28·4 ,,
0	100	,, 3 ,,	24 ,,

Refractometer Reading—*Butyro-refractometer.*—*Mansfeld* gives the following results obtained with the butyro-refractometer at 40° C. :—

Fat.	Refractometer Reading.
Lard from leaf, ...	51·2
,, exterior part of leaf, .	50·7
,, stomach, . . .	50·4
,, intestines, . . .	49·0
,, back, ...	50·2
,, ,, ...	50·4
,, ,, ...	48·6
American lard, ...	51·4
,, ,, ...	51·9
Beef fat, ...	49·0
Horse fat, ...	53·7
Coconut oil, ...	35·5
Cotton-seed oil, ...	61·0

Oleo-refractometer.—*Jean*[2] recommends a parallel determination of deviation of both the fat and liquid fatty acids separated by Sear's method (*q.v.*). He obtained the following results with different fats at 45° C. :—

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[1] *Oils, Fats, and Waxes*, 1895, 471.

[2] *Bull. Soc. Chim.*, 1895, xiii., 780.

Fat	Original Lard.	Liquid Fatty Acids.
Typical lard,	−12·5	−30
Steam lard,	−13	−30
Beef fat,	−17	−40
Pressed beef fat,	−34	...
Cotton-seed "stearine,"	+25	+20
,, oil,	...	+10
Sesamé oil.	...	−18
Earth-nut oil,	...	−15
Lard + 20 per cent. earth-nut oil,	−8·0	−23
,, ,, ,, cotton-seed oil,	−6·0	...

Dupont[1] shows that the oleo-refractometer reading varies with the part of the animal whence the fat was derived. He gives the following results obtained with American lards of known purity :—

Lard.	Oleo-refractometer.	Iodine Value.
European (typical),	−12·5	59
American leaf,	−11·5	58
,, back,	− 5·0	64
,, belly,	− 7·0	62
,, head,	− 7·0	63
,, foot,	− 4·0	65
,, intestine,	−11·0	60
,, rancid,	− 7·0	63
,, sour,	− 6·5	64
,, mixed,	− 7·0	63
,, lard oil,	− 1·0	80
,, ,,	0	82

From the results of these different chemists, it is evident that the refractometer reading should only be regarded as confirmatory evidence of adulteration.

Detection of Vegetable Oils.—*Bömer's* method of determining the melting point of the phytosteryl acetate (*cf.* p. 173) appears the most promising for the detection of very small proportions of vegetable oils in lard.

Soltsien[2] finds that American lards from pigs fed upon cotton-seed meal give Halphen's and Becchi's test, but do not contain phytosterol, and he considers Bömer's test as decisive.

Cotton-seed Oil and "Stearine."—These will be indicated by an increase in the specific gravity and in the iodine value of the fat and "liquid" fatty acids, by a marked reduction of silver nitrate in Becchi's test, by Halphen's reaction, and by the nitric acid test, considered in conjunction with the phytosterol tests.

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[1] *Bull. Soc. Chim.*, 1895, xiii., 775.

[2] *Analyst*, 1902, xxvii., 95.

Earth-nut Oil.—Determination of arachidic acid, iodine value of liquid fatty acids and phytosterol tests.

Maize Oil.—Iodine value of fat and fatty acids, phytosterol tests, and large amount of linolic tetrabromide obtained from the liquid fatty acids by Farnsteiner's method.

Sesamé Oil.—Baudouin's test, phytosterol tests, iodine value of fat and liquid fatty acids.

Coconut Oil.—Increased saponification value, with lower iodine value, phytosterol tests, Reichert value, and extended Reichert value, Polenske value, and solubility in alcohol of different strengths (see *Coconut oil*).

Detection of Beef Fat and other Animal Fats.—It is frequently a difficult problem to determine whether a sample of lard has been adulterated with beef fat, owing to the natural variation in the fat taken from different parts of the pig.

Hehner and Mitchell's method of determining the stearic acid in the mixed fatty acids considered in conjunction with the iodine value and melting point of the fat and fatty acids, will probably be found on extended experience to afford reliable information. At present, however, reliance is placed on the results of crystallisation of the fat from ether.

Belfield's Process.—A qualitative test for the detection of beef fat in lard was based by *Belfield*[1] on the difference in the form of the crystals obtained on allowing a saturated solution of the fat in ether to slowly evaporate from a tube closed with a plug of cotton-wool.

When examined under the microscope, the crystals obtained from ordinary lard have the appearance shown in Fig. 105 (plate), whilst those from flare lard appear as in Fig. 106 (plate), and mixtures of lard and beef fat yield crystals intermediate in their shape (Fig. 107, plate).

It was pointed out by *Hehner* that on continually recrystallising lard crystals from ether, they eventually become almost indistinguishable from the crystals of beef fat. Some light has been thrown on this by the experiments of *Hehner* and *Mitchell*,[2] who determined the amount of stearic acid in the successive deposits. A lard with an iodine absorption of 57·5, and containing 16 per cent. of stearic acid in its fatty acids, was crystallised from ether in the proportions used in the Belfield test. The deposit, which showed the usual chisel-shaped crystals, contained 32·4 per cent. of stearic acid in its fatty acids, whilst the fatty acids in residue from the filtrate contained 15 per cent.

On recrystallising the main deposit crystals, which were needle-shaped, but still having the chisel-shaped ends, were obtained. These contained 47·6 per cent. of stearic acid in their fatty acids, whilst the fatty acids from the glycerides in the solution contained 17·23 per cent.

A third crystallisation yielded a deposit whose fatty acids contained 59 per cent. of stearic acid, whilst the fat in solution contained 33·2 per cent. The form of these crystals was practically identical with those from beef stearine.

From this experiment *Hehner* and *Mitchell* concluded that the difference in the crystalline forms of the deposit from beef fat and from lard must be attributed to the presence of a larger proportion of stearic acid in the former, but *Kreis* and *Hafner*[3] found that it was due to the presence of distinctive glycerides.

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[1] *Analyst*, 1888, xiii., 70.

[2] *Analyst*, 1896, xxi., 328.

[3] *Ber.*, 1903, xxxvi., 2766; *Zeit. Nahr. Genussm.*, 1904, vii., 641.

Stock's Process.—*Stock*[1] has devised a process with the object of obtaining quantitative results from the Belfield test. He prepares two sets of standard mixtures from

A. { Pure lard melting at 34° C. to 35° C.
Beef stearin melting at 56° C.

B. { Pure lard melting at 39° C. to 40° C.
Beef fat melting at 50° C.

These mixtures contain 5, 10, 15, and 20 per cent. of the beef fat, and are intended for comparison with lards of unknown origin melting at 33° C. to 39° C., and 39° C. to 45° C. respectively.

The melting point of the sample is first taken by the capillary tube method, the tube being allowed to stand for twenty-four hours after filling. Assuming it to melt at 34° C., 3 c.c. of the melted fat are dissolved in 21 c.c. of ether (sp. gr. 0·720) in a stoppered cylinder, which is immersed in water at 20° C. to 25° C. At the same time, 3 c.c. of each of the "A" mixtures are treated in the same manner, and the five cylinders cooled to 13° C., and allowed to stand at that temperature or lower for twenty-four hours. The ether is then decanted from the deposits, and 10 c.c. of fresh ether at 13° C. introduced into each cylinder, which is then closed and shaken. After the deposits have again subsided, the washing is repeated, the contents of the cylinders transferred to weighed beakers, and the deposits dried at 40° C., and weighed. The standard weight nearest to the weight of the lard deposit is used as the basis for calculating the proportion of beef fat present.

The presence of the characteristic beef fat crystals in the deposit must be confirmed by microscopical examination.

Stock found that in practice the "B" standards were usually required. The following table gives the results that he obtained with his standards :—

"*B*" *Standards.*

Percentage Composition.		Melting Point.	Ether-washed Deposit.	Difference of Ether-washed Deposit.
Lard.	Beef fat.	° C.	Milligrammes.	Milligrammes.
5	95	40·2	43	...
10	90	41·0	81	38
15	85	41·6	122	41
20	80	42·4	181	59

In Stock's opinion no normal lard melting below 39° C. would yield an ether-washed deposit of more than 11 milligrammes by this process.

The following results were obtained with pure lards of different origin :—

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[1] *Analyst*, 1894, xix., 2.

Pure Lards.

Origin.	Melting Point.	Ether-washed Deposits.
	° C.	Milligrammes.
1. Leaf lard, . . .	45·8	146
2. Belly „	39·0	11
3. Back „	34·5	None
4. Leaf „	45·5	114
5. Soft „	34·0	6
6. Hard „	42·5	83
7. „ „	41·0	90

The following samples of unknown origin were judged to contain beef fat in the proportions stated :—

	Melting Point.	Ether-washed Deposit.	Beef Fat Reported.
	° C.	Milligrammes.	
Commercial lard, .	34·6	50	7
„ „ .	39·0	52	6
„ „ .	40·2	73	9 to 10
„ „ .	40·3	102	12
„ „ .	38·8	56	7
„ „ .	36·2	38	5
„ „ .	41·8	32	5
„ „ .	37·6	36	5

In the case of a leaf lard containing beef fat, *Stock* relied upon the initial deposition temperature as an indication of the proportion of beef fat, having found that lard stearine began to deposit at 13° C., and beef fat about 3° higher.

He also took into account the crystalline form, and recrystallised the deposit from successive portions of 5 c.c. of ether cooled gradually to 14° C., and calculates the amount of the final deposit as beef fat melting at 56° C.

In the light of Hehner and Mitchell's experiments (*supra*) there appears to be considerable risk of lard stearine being taken for beef stearine after continued crystallisation in this manner.

Dunlop [1] also found that by repeated crystallisation of the feathery crystals from beef fat they were finally converted into flat crystals similar to those from lard. The test must, therefore, be used cautiously and only regarded as confirmatory evidence.

Polenske's Method.—This depends upon the fact that the difference between the melting and solidification points (" difference value ") is fairly constant for the same kind of fat, but varies greatly in the case of some other kinds of fat.

[1] *J. Soc. Chem. Ind.*, 1906, xxv., 459.

The clear melted fat is dried at 102° to 103° C. in a current of carbon dioxide, then introduced into a U-shaped capillary tube, which is left in contact with ice for 24 hours. The tube is attached to a standard thermometer, which is gradually heated in a mixture of glycerin and water from 20° C., first at the rate of 2° C. per minute until within 5° C. of the melting point, and then at 0·75° C. per minute. The melting point is the temperature at which the fat becomes perfectly clear.

The solidification point is determined by placing a flat-bottomed tube containing a column of the fat 17 cm. high and 1·8 cm. in diameter, in a wider tube to form an air chamber, and immersing the latter in a water-bath. The melted fat is stirred mechanically with a rotating nickel stirrer, and the solidification point is the temperature at which two black marks on the wall of the tube cease to be visible. Duplicate determinations should agree within 0·2° C.[1]

In the case of beef fat *Polenske* found the difference values to vary from 12·8 to 14·7, whilst lard showed differences of 19 to 21. He, therefore, concluded that lards showing a difference value of 18·5 were adulterated. Goose fat showed difference not exceeding 17, whilst butter fat gave values of 11·7 to 14·3.

Bömer and *Limprich*[2] have shown that *Polenske's* "difference values" depend mainly upon the differences of the glycerides in the respective fats (see p. 677). The α-palmito-distearin of lard shows a value of 18·4, whereas the β-palmito-distearin of beef and mutton fat has a value of 11·8. Tristearin has a difference value of 19·7, but its proportion in beef fat (1 to 2 per cent.) is insufficient to outweigh the greater proportion of α-palmito-distearin in lard.

In *Bömer's* experience the method is capable of detecting about 20 per cent. of beef fat and 15 per cent. of mutton fat in lard, but sufficient time must be allowed for the stable form of the glyceride to solidify before applying the test.

Bömer's Method.[3]—This is based upon the fact that the distinctive glyceride of lard, α-palmito-distearin melts at a temperature differing by 5·2° C. from its separated fatty acids, whereas in the case of β-palmito-distearin the corresponding glyceride in beef and mutton fats, the difference is only 0·1° C.

The test is applied by leaving a solution of 50 grms. of the melted lard in 50 c.c. of ether at about 15° C. until crystals deposit. These are pressed between filter paper, recrystallised from 50 c.c. of ether, and again pressed. Should the melting point now be less than 61° C. the crystallisation must be repeated until that melting point is reached. After separation of the fatty acids from part of the glycerides the melting points of both glycerides and fatty acids are determined.

Lards with glycerides melting between 61° and 65° C. are to be regarded as adulterated when the melting point of the glycerides added to twice the difference between the melting points of the glycerides and their fatty acids is less than 71° C.

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[1] *Arbeit Kaiserl. Gesundheitsamt*, 1907, xxvi., 444.

[2] *Zeit. Nahr. Genussm.*, 1913, xxv., 367.

[3] *Zeit. Untersuch. Nahr. Genussm.*, 1913; xxvi., 559; 1914, xxvii., 153.

In the case of glycerides melting between 60° and 61° C., the presence of beef or mutton fat or of hydrogenated oils (*q.v.*) is indicated when the difference between the melting points is less than 5° C., and in the case of glycerides melting from 65° to 68·5° C. when the difference is less than 5° C.

Abnormal results due to the presence of fats such as shea butter may be checked by the phytosteryl acetate test. This also applies to hydrogenated vegetable oils, which may lower the difference in the melting points of lard to a greater extent than beef fat.

Feeding pigs upon abnormal amounts of coconut, maize, sesamé, and cotton-seed cake causes the lard to contain a smaller proportion of α-palmito-distearin and more stearo-dipalmitin than ordinary lard, but does not interfere with the detection of beef fat by this method.

Sprinkmeyer and *Diedrichs*[1] find that *Bömer's* method will usually detect about 5 per cent. of beef or mutton fat in lard.

MUTTON FAT (MUTTON TALLOW).

Recorded Values.

Mutton Tallow.

Specific Gravity.	Saponification Value.	Iodine Value.	Melting Point.	Authority.
° C.				
0·937-0·953 at 15°	...	34-37·7	47-49	Dieterich.
0·858 at 100°	195·2	32·7	...	Thoerner.
...	...	48·2-61·3	...	Hehner & Mitchell.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value of Liquid Fatty Acids.	Molecular Equivalent.	Authority.
° C.	° C.			
49	41	...	...	Thoerner.
33·8-45·6	...	...	276·1	Hehner & Mitchell.
...	...	92·7	...	Wallenstein & Finck.
...	Dalican's Test. 40·1-48·3	...	...	Lewkowitsch.

The fat rendered from the adipose tissue of the sheep varies greatly in its consistency, according to the part of the animal from which

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[1] *J. Soc. Chem. Ind.*, 1914, xxxiii., 563.

it is derived. Thus the fat obtained from the ham and breast is semi-solid at the ordinary temperature, whilst that from the back, neck, and kidneys (tallow) is very hard.

This difference appears to depend very largely upon the proportion of stearic acid present in the fat, judging by the results of *Hehner* and *Mitchell*,[1] who obtained the following results with fat from different parts of the same sheep :—

Fat from	Stearic Acid in Total Fatty Acids.	Stearic Acid in Saturated Fatty Acids (calculated).
	Per cent.	Per cent.
Back, . . .	24·8	78
Neck, . . .	16·4	36
Breast, . .	1·0	3
Ham, . . .	none	none
Kidney, . .	26·5	58

The variation in the chemical and physical characteristics of fat from different parts of the animal is shown in the following table of results :—

Description.	Melting Point.		Solidification Point of Fatty Acids.	Saponification Value.	Iodine Value.	Authority.
	Fat.	Fatty Acids.				
Two sheep—Fat from	°C.	°C	°C.			
Kidneys, . . .	54-55	56·2-56·5	51·9-51·9	194·8-195·2	...	Moser, quoted by Lewkowitsch.[2]
Caul and intestines, .	52-52·9	54·9-55·8	50·4-50·6	194·6-194·8	...	,,
Adipose tissue, .	49·5-49·6	50·7-51·1	43·7-46·2	194·2-194·4	...	,,
Scotch sheep, 18 months old—Fat from						
Back, . . .	...	41·4	...	...	61·3	Hehner and Mitchell.[3]
Neck, . . .	...	42·2	...	...	48·6	,,
Breast, . . .	...	33·8	...	...	58·2	,,
Ham, . . .	...	40·8	...	...	50·6	,,
Kidneys, . . .	...	45·6	...	...	48·2	,,

Mutton fat has a characteristic odour, much more pronounced than that of beef fat. On crystallisation from ether it yields a deposit of crystals closely resembling those obtained from beef stearine (see *Lard*).

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[1] *Analyst*, 1896, xxi., 327.

[2] *Oils, Fats, and Waxes*, 485.

[3] *Analyst*, 1896, xxi., 327, 328.

RABBIT'S FAT.

Recorded Values.

Rabbit's Fat.

Origin.	Specific Gravity.	Acid Value.	Saponification Value.	Iodine Value.	Hehner Value.	Reichert-Meissl Value.	Melting Point.	Authority.
							° C.	
Tame rabbit,	0·861 at 100° C.	...	...	...	95·47	2·64	44-46	Drumel.[1]
						Reichert Value.		
,,	0·9342 at 15° C.	6·20	202·6	69·6	...	2·8	40-42	Amthor & Zink.[2]
Wild rabbit,	0·9363	7·20	199·3	99·8	...	0·7	35-38	,,

Fatty Acids.

Origin.	Specific Gravity at 15° C.	Melting Point.	Solidification Point.	Saponification Value.	Iodine Value.	Butyro-refractometer at 40° C.	Authority.
		° C.	° C				
Tame rabbit,	...	48-50	39-41	...	...	36	Drumel.
,,	0·9264	44-46	37-39	218·1	64·4	...	Amthor and Zink.
Wild rabbit,	0·9426	39-41	35-36	209·5	101·1	...	,,

Rabbit's fat is of a white or yellowish-white colour. It has a characteristic odour, and a consistency somewhat less than that of lard.

As in the case of other wild animals, the iodine value of the fat of the wild rabbit is much higher than that of the tame rabbit.

TALLOW.

The terms " tallow " and " suet," especially the former, are often used indiscriminately to denote both the solid adipose tissues of various quadrupeds (more particularly the ox and sheep), and the fatty matters thence reduced by suitable treatment so as to separate them from the nitrogenous cellular tissue. Preferably, however, the term " suet " should only be applied to the untreated animal fatty tissues, whilst the word " tallow " should only imply the fatty matters thence extracted and freed from cell walls, etc. In this sense " tallow " includes the rendered fats obtained from the ox, sheep, goat, stag, and other quadrupeds, excluding the horse and hog, the fats from which are generally known as " horse-grease " (mare's grease) and " lard " respectively. The hardness of the substance varies according to the breed, age,

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[1] *Bull. de l'Ass. belge Chim.*, 1896, ix., 323.

[2] *Zeit. anal. Chem.*, 1897, xxxvi., 1.

and sex of the animals from which the tallow is obtained. The food and climate also produce variations; whilst, as in the case of hog's lard, the consistency of the product differs considerably with the part of the carcase furnishing the fatty tissue. These variations, however, so far as is known, do not affect the general character of the fat as regards its constitution; whether harder or softer, it essentially consists of glycerides of oleic, stearic, and palmitic acids, the former being present in the larger proportion the softer the fat.

Grades of Tallow.—In the trade there are various grades, in many cases known by special names either denoting the country from which the material is shipped ("River Plate tallow," "Australian tallow," "Russian tallow," etc.), or given for some other reason—*e.g.*, P.Y.C. tallow = Petersburg yellow candle (or prime yellow candle), a particular quality irrespective of source; "Prime Butchers' Association tallow," or "North American," mostly shipped from New York; "Western," imported from New Orleans; "tripe tallow" and "town tallow," grades usually softer and somewhat inferior because of admixture with waste dripping, kitchen grease, and other similar materials.

According to *Shukoff*,[1] the following commercial varieties are known in Russia :—*Benzine bone fat*, solidifying at 40° to 42° C., and containing up to 4 per cent. of water and impurities; *white natural bone fat* (*Petrograd*) containing 0·3 to 1·5 per cent. of water and impurities, and 20 to 30 per cent. of free acids, solidifying at 40° to 45° C.; *leather fat*, with 2 to 4 per cent. of water, etc. (solidifying at 37·6° to 38·9° C.); *Town tallow II. A* (*Petrograd*), solidifying at 39·3° to 43·2° C., and containing 1 to 3 per cent. of water, etc.; *Town tallow I. A* (*Petrograd*), with water and impurities 0·5 per cent. (solidifying at 45° to 46·6° C.); *Orenburg mutton tallow* (which is obtained from sheep's tails), containing 0·8 per cent. of water, and solidifying at 42·4° C.; and *Southern mutton tallow*, with water 0·4 per cent., and solidification point, 46·8° C.

Melting and Solidification Points.—As a general rule, Russian tallows are characterised by their high solidification points, which are usually 45° to 46° C. in the case of Petrograd tallow, and 41° to 42° C. for bone fat.

The melting and solidifying points of other varieties of tallow vary considerably, from 41° to 51° C., having been recorded by different observers for the former, and a few degrees lower for the latter.

The melting point of the fatty acids obtained on saponification also shows great variations according to the degree of hardness (*i.e.*, the amount of solid fatty acids present) of the fat. In the case of tallow of good quality it is usually about 47° C.

Dalican's Test.—The solidifying point as determined by Dalican's process (p. 98), sometimes termed the "titre" of the tallow, affords the best criterion of quality, so far as such physical tests go.

In this test 44° C. represents a mixture of equal quantities of "stearic" and "oleic" acids, lower values being obtained when

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[1] *Chem. Rev. Fett Ind.*, 1901, viii., 229.

"oleic" acid preponderates, and higher ones when "stearic" acid is in excess.

On the Continent, it is often stipulated that the solidification point shall not fall below 44° C. when the tallow is intended for candlemaking; whereby not only are the softer genuine (or comparatively so) tallows excluded, but also those largely adulterated with such substances as cotton-seed oil, cotton-seed stearine, Yorkshire grease, stearine from distilled grease, etc., as the presence of these materials tends to lower the melting point of the mixed fatty acids obtained.

Wool-grease and Yorkshire grease products are especially objectionable in this connection, because they contain more or less considerable quantities of cholesterol, hydrocarbons, and other unsaponifiable substances, which not only directly diminish the amount of "stearic" acid present, but also further diminish the quantity of solid fatty acids obtainable by pressing, since they interfere with the proper "seeding" or crystallisation of the press cake (*vide* p. 722). The determination of these unsaponifiable matters in tallow adulterated therewith, is carried out as described on p. 169.

Specific Gravity.—The specific gravity of tallow at 15° C. ranges from about 0·925 to 0·940, values of 0·925 to 0·929 being obtained with beef tallow, and somewhat higher ones (0·937 to 0·940) with mutton tallow (*Hager*). Slightly higher values, up to 0·952, were obtained by *Dieterich*.

Free Fatty Acids.—Fresh tallow contains very little free fatty acid; but tallow that has become more or less rancid often contains considerable amounts, up to 12 per cent. (calculated as oleic acid); 25 per cent. was found by *Deering* in a sample six years old, and still higher proportions by *Shukoff* in samples of Russian tallow (*supra*).

When tallow is not particularly rancid, and yet contains a considerable amount of free acid, it is very probable that it has been adulterated with distilled "stearine" (largely consisting of free fatty acids).

Saponification Value.—This usually lies between 193 and 198, corresponding with a saponification equivalent of 283 to 293, and a mean molecular equivalent of fatty acids of about 276 (palmitic acid = 256; oleic acid, 282; stearic acid, 284).

Iodine Value.—The iodine number has been found by different observers to lie between 35 and 45, with an average of about 40; since pure olein has the iodine number 86·2, this indicates an average amount of olein of somewhat less than 50 per cent. (about 46), and a proportion of solid glycerides of somewhat above 50 per cent. (about 54).

According to the author's experience, in the absence of adulterations the determination of the iodine value is a useful test of quality for candle-making purposes, the proportion of solid fatty acids obtainable being greater the less the iodine absorption; but when pressed coconut oil or palm-kernel oil has been added, the iodine number is reduced without a corresponding increase in amount of solid fatty acids of high melting point obtainable; and the same remark applies to wool-grease, wool stearine, and similar substances.

In the case of coconut and palm-kernel oils the Polenske value (pp. 244, 659) will afford evidence of the adulteration.

When circumstances permit, the best indications as to adulterations of this kind are obtained by saponifying, separating the fatty acids, allowing them to crystallise, and expressing them in a small experimental laboratory press, determining the quantity and melting point of the pressed cake, and subjecting the expressed oleic acid to examination as regards its iodine absorption, elaidin reaction, amount of unsaponifiable matters present, and so on; samples of genuine tallow of different qualities being examined side by side in the same way.

Muter and *de Koningh*[1] recommend a process based on somewhat similar principles, where the solid and liquid fatty acids are separated by conversion into lead salts and solution of lead oleate, etc., by ether, wherein lead stearate and palmitate are but sparingly soluble. By carrying out the saponification and subsequent processes in a uniform prescribed way, the quantity and characters of the liquid fatty acids ultimately separated from the soluble lead salt afford useful indications respecting adulteration. Thus, they found that the iodine value of the liquid acids obtainable from pure tallow was uniformly close to 90, or substantially identical with the theoretical value of pure oleic acid. Lard, on the other hand, gave liquid acids possessing a distinctly higher iodine value, close to 93, whilst the liquid acids from cotton-seed oil gave a still higher iodine value, near to 135 (see p. 148).

Rancid Tallow.—Tallow that has become rancid by keeping generally whitens during the process. Owing to the large amount of decomposition with formation of free fatty acids that occurs (*supra*), such tallow is unsuitable for lubricating purposes. Moreover, the by-products of the decomposition cause soap made from such tallow to "work foxy," or change in colour to brownish-red, so that for milled or other toilet soaps intended to be white or tinted delicate shades, such tallow should be avoided in the manufacture of the "stock soap" used.

Adulteration of Tallow.—Tallow is frequently adulterated with foreign substances, such as cotton stearine, wool-grease and Yorkshire grease, and the stearines thence obtained by distillation and pressure, bone-grease, together with solid non-fatty matters such as paraffin wax, China clay, whiting, starch, etc., the presence of which is easily recognised by applying a solvent and filtering.

According to *Williams*,[2] cotton-seed *oil* is often used as an adulterant in the case of softer tallows. These substances are detected by applying the tests described under the respective headings.

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[1] *Analyst*, 1889, xiv., 61; 1890, xv.

[2] *J. Soc. Chem. Ind.*, 1888, vii., 186.

FATS OF WILD ANIMALS AND BIRDS.

The following analytical results were obtained by *Amthor* and *Zink*[1] in their examination of the fat of different animals and birds, and of certain allied tame species :—

Fats of Wild Animals and Birds.

Fat of	Specific Gravity at 15° C.	Saponification Value.	Hehner Value.	Iodine Value.	Reichert Value.	Melting Point.	Solidification Point.	Acid Value.
						° C.	° C.	
Dog, . .	0·9229	195·4	95·65	58·5	0·57	37·5-40	21-23	1·79
Fox, . .	0·9412	191·7	...	79·7	1·30	35-40	24-26	5·90
Badger, . .	0·9226	193·1	96·0	71·3	0·36	30-35	17-19	5·30
Chamois, .	0·9697	203·3	...	25·0	1·80	54-56	42-43	3·20
Domestic cat, .	0·9304	190·7	96·0	54·5	0·90	39-40	24-26	2·30
Wild cat, .	0·9304	199·9	...	57·8	2·5	37-38	26-27	9·30
Pine marten, .	0·9345	204·0	93·0	70·2	1·10	33-40	24-27	12·65
Polecat, . .	...	...	...	62·8	...	...	...	...
Hare, . .	0·9349	200·9	95·2	102·2	1·59	35-40	17-23	2·73
Tame duck, .	...	...	...	58·5	...	36-39	22-24	...
Wild ,, .	...	198·5	...	84·6	1·30	...	15-20	...
Turkey, . .	0·9241	193·5	...	66·7	1·00	33-40	21-27	1·50
Blackcock, .	0·9220	200·5	...	81 15	...	...	...	4·00
,, .	0·9296	201·6	...	121·1	2·10	...	...	5·90
Pigeon, . .	...	...	...	82·3	...	...	...	...
Starling, .	...	209·2	...	83·7	...	30-35	15-18	...

Fatty Acids.

Fat of	Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Melting Point.	Solidification Point.
				° C.	° C.
Dog, . . .	0·9278	199·15	50·15	39-40·5	34·5-35·5
Fox, . . .	0·9492	205·7	65·4	41-43	36-37
Badger, . .	0·9230	193·7	73·0	34-36	28-30
Chamois, . .	0·9546	206 5	24·4	57-58	51-52
Domestic cat, .	0·9251	...	54·8	40-41	35-36
Wild cat, . .	0 9366	203·8	58·8	40 41	36-37
Pine marten, .	...	...	53·0	39-43	35-37
Pol cat, . .	...	...	60·6	34-40	36-37
Hare, . . .	0·9361	209 0	93·3	44-47	36-40
Tame duck, . .	...	...	...	...	...
Wild ,, . .	...	...	...	36-40	30-31
Turkey, . .	0·9283	200·8	64·6	38-40	32-34
Blackcock, . .	0·9385	210·1	70·7	38-39	31-32
,, . .	0·9374	199·3	120·0	30-33	25-28
Pigeon, . . .	...	...	...	38-39	33-34
Starling, . .	...	...	79·4	38-39	30-31

Amthor and *Zink* found that, as a rule, a high specific gravity was accompanied by a high melting point and a low iodine value. The

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[1] *Zeit. anal. Chem.*, 1897, xxxvi., 1.

iodine value and generally the acetyl value (determined by Benedikt's original method) were lower in the case of domestic animals than in that of the corresponding wild animals. In like manner the fat of domestic birds was lard-like, whilst that of the related wild bird was oily and had a high iodine value.

In four instances the fats had marked drying properties, becoming solid in a short time when exposed in a thin film upon glass. This was the case with the fat of the hare, wild rabbit, and wild boar, and, to a less extent, with that of the blackcock.

Fox fat differed from the fat of the cat and dog in its higher iodine value and specific gravity, but more particularly in its high acetyl value.

Polecat fat was quite liquid, and showed lower values than the fat of the marten.

The fats of the dog and cat resembled lard in appearance, and in most of their physical and chemical properties. Of the different bird fats examined, that of the blackcock was notable for its high iodine value and drying properties. When spread in a thin layer upon glass it gradually formed a sticky varnish. After ninety-five days the iodine value had fallen to 29·7.

CLASS X.—SPERM OIL CLASS.

ARCTIC SPERM OIL. BOTTLENOSE OIL.

Recorded Values.

Arctic Sperm Oil.

Specific Gravity at 15·5° C.	Saponification Value.	Reichert Value.	Iodine Value.	Maumené Test.	Alcohols.	Authority.
				° C.	Per cent.	
0·8808	126	1·4	...	41-47	37·41	Allen.
...	123-134	...	80·4	42	...	Archbutt.
				Spec. Temp. Reaction.		
0·8799	130·4	...	82·1	93	36·32	Thomson and Ballantyne.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
° C.	° C. Dalican's Test.		
10·3-10·8	8·3-8·6	82·2-83·3	Lewkowitsch

This oil obtained from the bottlenose whale, *Hyperöodon rostratus*, closely resembles sperm oil in its physical and chemical characteristics, but is less valuable as a lubricant.

Lewkowitsch[1] found the unsaponifiable matter (about 34 per cent.) to consist of alcohols with the following characteristics:—Melting point, 23·5° to 26·5° C.; solidification point, 21·7° to 22·0° C.; and iodine value, 64·8 to 65·2.

A sample of the oil examined by *Thomson* and *Ballantyne* contained 0·42 per cent. of free fatty acids.

SPERM OIL.

Recorded Values.

Sperm Oil.

Specific Gravity at 15·5° C.	Saponification Value.	Reichert Value.	Iodine Value.	Acetyl Value.	Refractive Index at 15° C.	Maumené Test.	Authority.
						°C.	
0·875-0·884	..	1·3	..	..	..	45-47	Allen.
0·8808	132·5	..	81·3	..	..	..	Thomson and Ballantyne.
..	..	..	84	..	..	51	Archbutt.
..	125·2-132·6	..	..	4·49-6·43	..	..	Lewkowitsch.
0·882 at 15°	..	..	..	..	1·4675	..	Procter.
0·886	..	..	78·7	..	..	..	Sherman and Snell.
..	..	..	79·85	..	1·4649-1·4669	..	Vulté and Logan.

Fatty Acids.

Specific Gravity at 15·5° C.	Melting Point.	Solidification Point.	Mean Molecular Equivalent.	Iodine Value.	Authority.
	°C.	°C.			
0·899	..	..	281-294	..	Allen.
..	13·3	..	305	88·1	Williams.
..	..	Dalican's Test. 11·1-11·9	..	83·2-85·6	Lewkowitsch.
0·893-0·89	..	6·2-13·6	..	..	Blakeley and Reilly.

Origin.—Two varieties of sperm oil proper are obtained from the Cachalot whale (*Physeter macrocephalus*); one from the blubber by the ordinary processes of rendering, the other from the "head matter" or contents of the cranial cavities. This latter usually contains a larger proportion of solid constituents, so that on standing it soon becomes more or less pasty or semi-solid from the separation of spermaceti.

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[1] *Oils, Fats, and Waxes*, 523.

This solid constituent also deposits from the blubber oil on standing and chilling, but to a somewhat lesser extent.

Sperm oil thus freed from spermaceti is pale yellow and nearly odourless when prepared at comparatively low temperatures from fresh blubber, etc.; although, like all other fish and blubber oils, possessed of a marked unpleasant smell and darker colour when extracted by greater heat from partly decomposed blubber.

Sperm oil is in reality a liquid wax, being composed of various alcohols in combination with acids of the oleic series, of which physetoleic acid is said to be one. It is almost, if not quite, free from glycerol (*Allen*, *Lewkowitsch*). On saponification it yields 60 to 63 per cent. of fatty acids, and 38 to 41 per cent. of alcohols.

Lewkowitsch made experiments to separate the alcohols by fractional distillation, and proved the absence of dodecatyl and pentadecyl alcohol. He also found that, in the main, the alcohols of sperm oil belong to the ethylene series and have high iodine values.

Blakeley and *Reilly* [1] found that the isolated alcohols had an iodine value of 63·9 to 74·1, melted at 20·0° to 27·0° C., and yielded an acetate with a saponification value of 189·5 to 216·0.

Properties and Tests of Purity.—Sperm oil has but little tendency to become rancid, or to "gum" and thicken by exposure to the air, whilst its viscosity is but little affected by change of temperature, so that it forms a valuable lubricating oil.

The "flake test"—*i.e.*, the temperature at which solid matter separated from the oil—was found by *Blakeley* and *Reilly* [1] to vary from 3·3° to 10·0° C.

Specific Gravity.—This is remarkably low, resembling that of lubricating petroleum oils. Hence any notable addition of a foreign fatty oil would cause a rise in this value.

Viscosity.—The viscosity of sperm oil is affected less by temperature variations than that of most other oils, so that if other oils be present the efflux viscosity rates at different temperatures (*e.g.*, 15° C., 50° C., and 100° C.), will be considerably increased.

Free Fatty Acids.—As a rule, the proportion of free fatty acids in sperm oil is very small. Thus, *Deering* found samples of different quality to contain from 0·11 to 0·42 per cent. In some cases, however, oil of inferior quality contains considerably more, as, for instance, 0·78 per cent. recorded by *Sherman* and *Snell*, and 2·64 per cent. by *Thomson* and *Ballantyne*.

In experiments upon a large number of oils intended for burning in safety lamps of the Davy type it was found by *Blakeley* and *Reilly* (*loc. cit.*) that sperm oil containing from 1 to 4 per cent. of oleic acid caused a slight crust to form upon the wick of the lamp, but otherwise gave satisfactory results in burning, but the addition of 6 per cent. of free acid made the oil unsatisfactory. Hence, in their opinion the injurious effects of free acids upon a lamp oil have been over-estimated in the case of sperm oil. In judging as to the suitability of sperm oil

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[1] *J. Ind. Eng. Chem.*, 1917, ix., 1099.

as a lamp oil they lay stress upon the iodine value and refractive index, as well as upon the acidity and the other physical values.

Saponification Value.—The low saponification value of sperm oil is a valuable test of purity, since it is raised by the addition of fatty oils.

According to *Lobry de Bruyn*, however, mixtures of sperm, blubber, and mineral oils are sold as sperm oil, the mineral oil lowering the saponification value to the required extent.

Bromine Value.—According to *Vulté* and *Logan*, more bromine than iodine is absorbed by sperm oil as is shown by the following results :—

Bromine Absorption.	Bromine Addition.	Bromine Substitution.	Iodine Value Calculated from Bromine.	Iodine Value (*Hübl*).
54·6	52·3	2·27	79·81	82·3

Detection of Adulteration.—*Fatty oils* are detected by the increase in the saponification value, iodine value, and specific gravity, by the viscosity, and by determining the amount of glycerol, which should not be present in any appreciable quantity.

For the detection of liver oils, *Allen* recommends the colour reaction with sulphuric acid (see *Cod-liver Oil*), sperm oil giving only a brown coloration instead of a violet one in this test.

In many cases the iodine value may afford information of the addition of more unsaturated oils.

Mineral oils lower the saponification value and increase the amount of unsaponifiable matter.

CLASS XI.—VEGETABLE NON-GLYCERIDIC WAXES.

CARNAUBA WAX.

CIRE DE CARNAUBA. CARNAUBAWACHS. CEARAWACHS.

Recorded Values.

Carnauba Wax.

Specific Gravity.	Acid Value.	Ester Value.	Saponification Value.	Iodine Value.	Melting Point.	Unsaponifiable Matter.	Authority.
0·8500 at $\frac{90^\circ}{15{\cdot}5^\circ}$ °C.	4-8	76	80-84	...	°C. 85	Per cent. 54·8	Allen.
...	4	75	79	...	...	...	Hübl.
...	...	...	...	...	83-83·5	55	Stürcke.
0·995-0·999 at 15°	...	...	...	...	85-86 (*a*)	...	Schädler.
...	...	...	...	...	90-91 (*b*)	...	,,
...	...	...	...	13·5	...	...	Lewkowitsch.

(*a*) Freshly purified wax. (*b*) Old wax.

Carnauba wax is an exudation deposited upon the leaves of the wax palm (*Copernicia cerifera*), a tree that grows in Brazil, Venezuela, and other parts of South America.

According to *Stürcke*,[1] carnauba wax contains the following substances:—(1) A hydrocarbon (m.p. 59° to 59·5° C.); (2) an alcohol, $C_{27}H_{56}O$ (m.p. 76° C.); (3) myricylic alcohol, $C_{30}H_{62}O$ (m.p. 90° C.); (4) an acid, $C_{24}H_{48}O_2$ (carnaubic acid) (m.p. 72·5); (5) cerotic acid; (6) a hydroxy acid, $C_{19}H_{38}{<}^{CH_2OH}_{COOH}$.

Stürcke was unable to detect cerotic acid in the free state.

The crude wax is of a dirty greenish-grey colour and can be readily pulverised. It is practically tasteless, but has an odour recalling that of coumarin.

It is only partially soluble in cold alcohol, but readily dissolves in boiling absolute alcohol and in ether.

Carnauba wax is used in the manufacture of candles and of wax varnishes.[1] When used in admixture with paraffin fats, etc., for candles, it raises the melting point and imparts a characteristic polish.

The following table showing the melting points of mixtures of carnauba wax with paraffin wax and stearic acid, as determined by *Valenta*, is given by *Schädler*[2]:—

Percentage of Carnauba Wax (m.p. 85° C.).	Stearic Acid (m.p. 58·5°).	Paraffin Wax (m.p. 60·1°).	Paraffin Wax (m.p. 72·7°).
	Melting Point of Mixture.	Melting Point of Mixture.	Melting Point of Mixture.
5	69·75	73·90	79·10
10	73·75	79·20	80·56
15	74·55	87·10	81·60
20	75·20	81·50	82·53
25	75·80	81·70	82·95

Carnauba wax is sometimes used to adulterate beeswax. For the methods employed for its detection see *Beeswax*.

Formation of Beeswax.—A good deal of dispute has taken place at various times as to whether the wax of the bee, wasp, and similar insects is a distinct product of secretion due to their own special life action, or is simply originally present in the pollen and nectar of the flowers, etc., serving as their food, and is left on the removal of the other constituents by digestion or otherwise.

The latter view receives support from the fact that when bees are fed upon sugar only, they appear to be incapable of developing wax to any notable extent. On the other hand, although the character of bee food necessarily varies much in different parts of the world, yet the chemical constitution of beeswax does not differ anything like so widely. Thus, *Hehner*[3] found that samples of wax from different parts of Europe, Asia, South America, and Australia were all very similar in composition, consisting essentially of a mixture of about

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[1] Liebig's *Annalen*, ccxxiii., 283.

[2] *Technologie der Fette*, 884.

[3] *Analyst*, 1883, viii., 16.

CLASS XII.—ANIMAL WAXES: BEESWAX AND SPERMACETI CLASS.

BEESWAX.

Recorded Values.

Beeswax.

Origin.	Specific Gravity.	Acid Value.	Saponification Value.	Ester Value.	Iodine Value.	Melting Point.	Solidification Point.	Authority.
						° C.	° C.	
Yellow wax, . . .	0·8221 at $\frac{98° C.}{15·5° C.}$	...	...	...	...	63	60·5	Allen.
Chemically bleached, .	0·827 ,,	...	...	...	...	63·5	62	,,
Air bleached, . .	...	...	...	...	...	63·0	61·5	,,
...	...	20	95	75	...	...	...	Hübl.
Yellow wax, . . .	0·962-0·966 at 15°C.	16·8-20·6	87·8-96·2	71·8-75·6	8·8-10·7	...	...	Dieterich.
White wax, . . .	0·964-0·968 ,,	18·6	90·4-91·4	71·8-72·8	...	...	...	,,
Indian (2), . . .	...	6·0, 6·1	82·1, 83·3	76·1, 77·2	10	65, 66	...	Buchner.
Chinese (7), . . .	...	5·3-9·7	90·2-120·2	84·6-111·4	...	62-66	...	,,
Morocco, ...	...	19-21	92-98	73-76	...	...	...	Kayser.
Black wax (Dutch Indies),	0·978	34·3	78·05	43·25	69·1	54	...	Bilts.
English, . . .	...	...	...	...	8·5 (average)	...	...	Glode Guyer.
Italian, yellow (24), .	0·961 -0·964	18·31-21·6	90·57-97·86	70·74-77·6	...	62·2-63·2	...	Prosio.
,, white (4), . .	0·9655-0·967	21·8-23·77	97·18-103·97	73·58-81·76	...	62·5-63·5	...	,,
Smyrna, yellow (2), .	0·961	19·38, 19·96	92·8, 94·6	73·95, 75·25	...	63·2, 63·3	...	,,
S. Domingo, yellow (1),	0·9625	19·87	96·80	76 93	...	62·0	...	,,
Mogadore, . . .	0·961	19·92	99·35	79·43	11·65	64-65	61	Buchner.
Italian, yellow, . .	0·961 -0·964	21-22	91-96	70-74	...	63-64·4	...	Funaro.

1 part of free cerotic acid to 6 of myricin (*vide infra*)—a result hardly compatible with the notion that the wax was originally present as such in the pollen and nectar of the wide variety of flowers, etc., furnishing the food of the bees in these different quarters of the globe.

Andaquia wax (wax of *Apis fasciata*, largely used for candle-making in South America) appears to be substantially identical with the ordinary beeswax of *Apis mellifera*; and the same remark applies to *Antilles wax* (*Apis fasciata ?*), and to *Madagascar wax* (*Apis unicolor*), although frequently beeswax of tropical and sub-tropical origin is darker coloured and less readily bleached than that produced in more temperate climates.[1]

The wax of the Eastern Archipelago, again, differs but little from that obtained from other sources, although mainly produced by a different species (*Apis dorsata*). There are, however, great differences between the black beeswax of the Dutch Indies and the ordinary varieties of wax (*vide infra*), though possibly this may not be entirely the genuine product of bees.

Preparation.—In order to obtain the beeswax, the combs are simply drained of honey, and then melted in hot water and stirred about, the wax collecting on the surface as an oily layer, which is removed after cooling and hardening. After being re-melted by means of dry heat (without water) and cast into blocks, the "virgin" wax is ready for the market.

A large proportion is used for various purposes without further treatment. For certain purposes, however, bleaching is necessary. This is effected either by exposure in thin shavings to the action of air and sunlight, or by means of chemicals, preferably dilute sulphuric acid and potassium bichromate (*cf.* Chap. XI.).

In the air-bleaching of wax a small proportion of fatty matter is often added, which apparently facilitates the process. A little turpentine is also occasionally used for the same purpose, the acceleration in this case being probably due to the formation of hydrogen peroxide in the oxidation of the turpentine by the atmospheric oxygen in contact with water.

Composition.—As was mentioned above, beeswax is, as a general rule, remarkably constant in composition, whatever its origin.

It consists mainly of free cerotic acid, $C_{27}H_{54}O_2$, and of myricin (myricyl palmitate, $C_{30}H_{61} . O . C_{16}H_{31}O$), together with smaller proportions of free melissic acid, $C_{30}H_{60}O_2$, of unsaturated fatty acids, and of cerylic and other alcohols.

In fifteen samples of genuine English wax examined by *Hehner* (*loc cit.*), the proportion of cerotic acid was found to vary from 12·15 to 15·91 per cent., the average being 14·4; whilst the amount of myricin ranged from 85·95 to 89·06, with an average of 88·09 per cent. The proportion of myricin to cerotic acid was thus as 6·117 to 1.

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[1] Wax from the vicinity of Bordeaux appears to be the variety most difficult to bleach; whether from some local peculiarity in the flowers frequented by the bees, or for some other reason, is unknown.

Similar results were subsequently obtained by *Hübl.*

According to *A.* and *P. Buisine*, beeswax contains about 13 per cent. of hydrocarbons, whilst *Kebler* found the proportion to vary between 12·5 and 14·5 per cent., and *Ahrens* and *Hett* found from 12·7 to 17·5 per cent. in different kinds of wax which they examined by Buisine's method.

Humble Beeswax.—*Sundvik*[1] examined the wax extracted from the comb formed by humble bees. About 30 grammes of wax, melting at 35° to 40° C., were obtained from 130 grammes of the comb by extraction with ether or chloroform.

The wax had an aromatic honey-like odour, but became rancid when bleached by exposure to the air. When treated with dilute potassium hydroxide solution, and repeatedly recrystallised from alcohol, a product melting at 74° to 75° C. was finally obtained. The acicular crystals, which had not the sticky nature of ordinary beeswax, agreed in composition with empirical formula, $C_{34}H_{70}O$.

Beeswax Oil.—This is a favourite medicinal remedy in Russia, obtained by distilling beeswax with lime, and rectifying the distillate over quicklime. On exposure to the air it becomes darker in colour, and, when chilled, yields a deposit consisting of hydrocarbons.

Greshoff and *Sack*[2] obtained, by dry distillation of beeswax, a hydrocarbon, $C_{15}H_{30}$ (b.p. 240° to 250° C.), which they regarded as identical with a compound isolated from petroleum. They also separated from the products of distillation substances with melting points of 63° and 56° C., which they concluded to belong to the olefine series.

Abnormal Waxes—*Indian and Chinese Beeswax.*—According to *Buchner*[3] Indian beeswax is hard, more glassy and more plastic than ordinary varieties of beeswax. Both Indian and Chinese wax showed very low acid values as compared with European samples (see *Table of Values*), so that their "ratio value" was considerably increased, and ranged from 11·06 to 17·9.

Black Beeswax.—The specimen of black beeswax examined by *Bilts*[4] was obtained from the Dutch Indies. It was soft and sticky and dissolved in chloroform, with the exception of a brown pollen dust to which *Bilts* attributed the dark colour. On treatment with petroleum spirit 80 per cent. of the wax was dissolved, the soluble portion consisting of a soft sticky mass with an acid value of 35·4. The chemical and physical contents of this wax are given in the *Table of Values.* They are so abnormal as to make it doubtful whether the sample was really genuine beeswax.

Ghedda Wax.—This is a very plastic, aromatic wax derived from British India. It gives very abnormal results. Thus, *Buchner*[5] states that he has frequently met with samples giving such figures as the following:—Acid value, 5·33; ester value, 88·35; and saponification value, 93·68.

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[1] *Analyst*, 1899, xxiv., 39.

[2] *Chem. Zeit. Rep.*, 1901, xxv., 177.

[3] *Chem. Centralbl.*, 1898, i., 151.

[4] *Ibid.*, 1898, i., 175.

[5] *Chem. Zeit.*, 1901, xxv., 37.

Properties of Beeswax and Tests of Purity.

Specific Gravity.—This is determined as described in Chap. v., the wax first having been melted in boiling water to remove any honey and then dried. In addition to the values in the table of constants the following figures have been recorded:—0·965 to 0·975 (*Hager*); 0·960 to 0·963 for yellow wax, and 0·973 for white wax (*Schädler*); all at 15° C.

The specific gravity is raised by the presence of paraffin, stearic acid, carnauba wax, Japan wax, and rosin, and lowered by lard and tallow.

Air-bleaching has but little effect upon the density, but the specific gravity of chemically-bleached wax is usually slightly higher than that of yellow wax.

Melting Point.—This is usually about 63° C., values varying between 61° and 65° C. having been recorded by different observers. Bleaching processes have very little effect upon the melting point of the wax.

The melted substance solidifies at one or two degrees lower than the temperature of complete fusion.

Solubility in Various Liquids.—Beeswax is readily soluble in carbon bisulphide and amyl alcohol; it dissolves in about 10 parts of boiling ether, less completely in cold ether, benzene, or petroleum spirit; in cold alcohol it is nearly insoluble, but dissolves in about 330 parts of boiling spirit.

In the case of most solvents, some parts of the wax dissolve much more freely than other portions. Thus, in the case of hot alcohol a small quantity of "cerolein" is left undissolved, consisting of fatty matter, principally palmitin and olein. The proportion of this constituent varies in waxes of different origin, but is never large, so that the presence of fatty glycerides in any quantity is only due to adulteration.

On treating the wax with limited quantities of hot alcohol the free cerotic and melissic acids are dissolved out, whilst the undissolved portion consists in the main of myricin (the palmitic ester of myricylic alcohol).

Critical Temperature of Solution.—*Crismer* obtained results varying from 129° to 133° C. for pure beeswax from different sources, whilst with alcohol of the same strength the following figures were given by other substances:—Cacao butter, 126°; ozokerite, 175°; carnauba wax, 154°; and paraffins of different constitution, 140° to 160° C.

Refractometric Examination.—According to *Prosio*[1] the refractometer reading taken in Zeiss's butyro-refractometer at 64° C., ranges from 30° to 32° in the case of genuine yellow or white wax, whilst waxes adulterated with stearic acid or ceresin give lower readings,

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[1] *Staz. Sper. Agrar. Ital.*, 1901, xxxiv., 122.

and those containing carnauba wax or resins, higher ones. This is illustrated by the following examples :—

	Amount Present.	Specific Gravity.	Acid Value.	Ester Value.	Saponification Value.	Hübl's Ratio.	Melting Point.	Refractometer Reading at 64° C.
	Per cent.						° C.	
Yellow wax,	Stearic acid, 5	0·9625	31·41	66·87	98·28	2·129	61·0	29·2
,, ,,	,, 30	0·962	71·55	30·0	101·56	0·419	54·5	24·2
White ,,	,, 6	0·966	30·25	68·35	98·6	2·26	61·7	29·8
,, ,,	,, 10	0·966	36·70	64·43	101·1	1·72	60·3	28·3
Yellow ,,	Ceresin, 35	0·959	...	...	...	...	63·5	28·0
Italian ,,	Carnauba wax, 15	...	...	...	...	...	...	not liquid at 64° C.
,, ,,	,, 8	...	...	...	...	...	...	32
Smyrna ,,	,, 50	...	...	...	...	...	...	34
Yellow ,,	Resin, 30	...	...	...	...	...	...	70
,, ,,	,, 15	...	...	...	...	...	...	49·5
,, ,,	,, 7	...	...	...	...	...	...	40·5

The following results were obtained with artificial mixtures showing normal Hübl ratios :—

Yellow beeswax,	50 parts,	Refractometer,	26°
Japan wax,	20 ,,	Melting point,	56·0° C.
Stearic acid,	4 ,,	Specific gravity,	0·958
Paraffin wax,	26 ,,		
Yellow beeswax,	20 parts,	Refractometer,	23·0°
Japan wax,	30 ,,	Melting point,	52·0° C.
Stearic acid,	5 ,,	Specific gravity,	0·959
Paraffin wax,	45 ,,		

Prosio considers that waxes giving a reading below 30° can be regarded as containing beyond doubt stearic acid, paraffin, or ceresin; whilst those ranging between 30° and 30·5° must be regarded as open to suspicion, and those between 30·5° and 32° probably free from stearic acid or paraffin. Readings exceeding 32° probably indicate resins or carnauba wax.

In order to prevent injury to the refractometer through heating the wax to its melting point, *Marpmann*[1] makes use of the fact that the refractive index of a mixture is the same as the sum of the indices of its constituents, and dissolves the beeswax in an ethereal oil with not too high a refractive index, such as clove oil or peppermint oil (see Chap. IV.).

Acid and Saponification Values.—*Becker* determined the saponification values of several specimens of beeswax under a pressure of

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[1] *Chem. Rev. Fett Ind.*, 1901, viii., 65.

5 cm. of mercury. He obtained the following results with wax and with various substances used in its adulteration :—

	Saponification Value.
Beeswax, ...	97-107
Paraffin wax, ceresin, . . .	0·0
Japan wax, ...	224·4
Carnauba wax, ...	93·1
Spermaceti, ...	108·1
Tallow, ...	196·5
Rosin, ...	194·3

From this it will be seen that the saponification value is lowered by the addition of paraffin, but raised by all the other substances. It would readily be possible, however, to prepare mixtures with the normal values (*vide supra*).

Hehner's Method.—From 3 to 5 grammes of the wax are heated with about 50 c.c. of methylated spirit that has been purified by distillation from caustic alkali, and the liquid titrated with standard alcoholic potassium hydroxide (of which 1 c.c. is equivalent to 0·3 to 0·4 c.c. of normal acid), phenol-phthalein being used as indicator. This gives the acid value. An excess of the alcoholic alkali is then introduced, and the contents of the flask boiled briskly under a reflux condenser for an hour, after which the excess of alkali is titrated back with standard sulphuric acid, the result giving the ester value (which *Hehner* expresses as myricin).

Hübl's Method.—From 3 to 5 grammes of the wax are boiled with 20 c.c. of 95 per cent. alcohol, and the liquid titrated with semi-normal alcoholic alkali, with phenol-phthalein as indicator. After the introduction of 20 c.c. of the standard alkali, the flask is heated for forty-five minutes on the water-bath and the excess of alkali titrated back with standard acid.

Buchner prescribes the use of absolute alcohol for the preparation of the alcoholic alkali, and of 96 per cent. alcohol for the treatment of the wax.

Eichhorn[1] has shown that by using amyl alcohol as a solvent the results are obtained in much shorter time than by Hübl's method. As any partial saponification is prevented, the acid values thus obtained are considerably lower than usual, whilst in the determination of the saponification value the saponification is more complete and the results considerably higher.

Cold Saponification.—*Henriques*[2] gives the following details of his method of cold saponification as applied to beeswax :—

Three grammes of the wax are dissolved in 25 c.c. of warm petroleum spirit and immediately titrated with semi-normal alcoholic sodium hydroxide, phenol-phthalein being used as indicator. This gives the

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[1] *Zeit. anal. Chem.*, 1900, xxxix., 640.

[2] *Zeit. angew. Chem.*, 1896, 221.

acid value. Twenty-five c.c. of alcoholic alkali are then added, and the liquid warmed and left for twenty-four hours in the cold, after which the excess of alkali is titrated. The ester value thus obtained added to the acid values gives the saponification value. The following results were thus obtained with samples of pure wax, the last of which had been bleached by a new method :—

	Acid Value.	Ester Value.	Saponification Value.	Hübl's Ratio.
Beeswax, yellow, . .	20·6	76·5, 76·8	96·6, 97·4	3·72
,, ,, . .	20·4	72·9, 73·9	93·3, 94·3	3·58
,, ,, . .	20·6	73·6, 75·1	94·2, 95·7	3·6
,, white, . .	22·4	76·1, 76·9	98·5, 99·3	3·41
,, ,, . .	28·4	76·6, 77·1	105·0, 105·5	2·71

The acid value and saponification value of three other substances used to adulterate beeswax were :—

	Acid Value.	Saponification Value.
Carnauba wax, A, . .	3·4	78·4
,, B, . .	7·0	83·4
Japan wax, . . .	...	221·2
Spermaceti, . . .	2·8	130·6

Buchner[1] concludes from the results of his experiments that the results obtained by cold saponification are much more accurate and constant than those yielded by Hübl's method. He finds that it is essential to use petroleum spirit boiling at 100° to 150° C., and that the lower the boiling point of the solvent the more incomplete the saponification.

Thus, he obtained the following comparative results in the examination of a sample of wax by the different methods :—

	Hübl's Method.	Cold Saponification.	
		Petroleum Spirit of Boiling Point 100° to 150° C.	Petroleum Spirit of Boiling Point 50° to 80° C.
Acid value, . . .	18·37, 18·50	19·48, 19·48	18·39, 19·48
Ester value, . .	75·98, 75·81	72·81, 72·81	53·60, 71·09
Saponification value, .	94·35, 94·31	92·29, 92·29	72·99, 90·57
Ratio, ...	4·15, 4·10	3·74, 3·74	2·91, 3·65

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[1] *Analyst*, 1898, xxiii., 11.

Hübl's Ratio.—It was first pointed out by *Hehner* that the free cerotic acid and the myricin in beeswax stood in a remarkably constant ratio to one another in different kinds of pure beeswax, this ratio averaging 1 : 6·117 in the case of English wax. Subsequently *Hübl* suggested calculating the relationship between the acid value and the ester value, and this method of expressing the results is now commonly known as the " Hübl ratio."

" *Ratio* " *of Pure Wax.*—In the case of pure yellow wax, *Hübl* found the ratio to vary from 3·6 to 3·8, the average being 3·7. The relationship of the acid and ester values in Hehner's results is very similar, averaging 3·59.

Prosio[1] calculated the ratios of the samples of wax examined by him (see *Table of Values*) to be as follows :—Italian (yellow), 3·40 to 4·06 ; Italian (white), 3·10 to 3·68 ; Smyrna wax, 3·7 to 3·88 ; and San Domingo wax, 3·87.

Allen has recorded a still lower ratio (2·96) for chemically bleached wax, whilst *Buchner* has obtained values of 2·70 to 3·20 for similar bleached products.

" *Ratio* " *of Substances used to Adulterate Beeswax.*—The following table gives some of the results obtained by *Hübl*, and at a later period by *Allen* :—

Substance.	Acid Value.	Ester Value.	Saponification Value.	Hübl's Ratio.	Authority.
Carnauba wax, .	4	75	79	19	Hübl.
,, .	4·8	76	80-84	9·5-19	Allen.
Japan wax, . .	20	200	220	10	Hübl.
,, . .	20	195	215	9·75	Allen.
Spermaceti, . .	Trace	63	63	...	,,
Tallow, . . .	4	191	195	48	Hübl.
Stearic Acid, .	195	0	195	...	,,
Rosin, . . .	110	1·6	112	0·015	,,
,, . . .	180	10	190	0·0556	Allen.

Hübl concluded from the results of his experiments with mixtures that (1) A saponification value lower than 92, with a normal ratio, would indicate the presence of paraffin wax or ceresin. (2) A ratio exceeding 3·8 would point to the presence of Japan wax, carnauba wax, or tallow, though the first would not be present when the acid value was less than 20. (3) In the presence of stearic acid or rosin the ratio would be lower than 3·8.

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[1] *Staz. Sper. Agrar. Ital.*, 1901, xxxiv., 122.

Buchner[1] considers that, given negative results for the qualitative tests for impurities, pure beeswax may give values falling within the following limits:—Acid value, 17·5 to 21; ester value, 70 to 78; saponification value, 87 to 99; and "ratio," 3·71 to 4·11. He also shows that, in the chemical bleaching of beeswax, the acid value may be raised at the expense of the ester value.

The effect of bleaching upon the acid and saponification values has also been studied by *A.* and *P. Buisine*, whose results are shown in the following table:—

Wax.	Melting Point	Acid Value.	Saponification Value.	Iodine Value.	Hydrogen yielded by 1 grm.	Hydrocarbons.
	° C.				C.C.	Per cent.
Yellow waxes, ...	63-64	19-21	91-95	10-11	52·5-55	13-14
Air-bleached waxes + 3 to 5 per cent. of tallow, . .	63·5-64	21-23	105-115	6-7	53·5-57	11-12
Yellow wax, ...	63·5	20·17	93·5	10·9	53	13·5
,, ,, air-bleached + 5 per cent. turpentine,	63·5	20·2	100·4	6·8	54·9	12·4
,, ,, bleached by H_2O_2, .	63·5	19·87	98·4	6·3	56·1	12·5
Yellow wax, ...	63	20·40	95·1	11·2	54·5	14·3
,, ,, bleached by animal charcoal .	63	19·71	93·2	11·4	53·6	13·3
,, ,, bleached by permanganate, .	63·7	22·63	103·3	2·6	...	...
,, ,, ,, . .	63·5	21·96	99·2	5·8	55·5	13·3
,, ,, bleached by bichromate, .	63·2	21·86	98·9	7·9	51	13·2
,, ,, ,, . .	64	23·43	107·7	1·1	53·6	11·8

It is easily possible to prepare mixtures of various substances giving normal "ratios," although being abnormal in other respects (see *Refractometric Examination, supra*). Hence too great reliance must not be placed on the determination of this value.

Buchner's Acid Value.—*Buchner*[2] recommends the following method of detecting foreign fatty substances in adulterated samples giving normal results with Hübl's method:—Five grammes of the wax are mixed with 100 c.c. of 80 per cent. alcohol, and the flask and its contents weighed. The alcohol is then boiled for about five minutes with constant shaking, and, after cooling, it is made up to the original weight with alcohol of the same strength, filtered, and 50 c.c. of the filtrate titrated with $\frac{N}{10}$ alcoholic potassium hydroxide, with phenolphthalein as indicator.

The following results were thus obtained with different waxes, fats, and mixtures:—

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[1] *Chem. Zeit.*, 1901, xxv., 21.

[2] *Ibid.*, 1895, xix., 1422.

Substance.		Acid Value.
Pure beeswax, yellow,		3·6 - 3·9
,, ,, white,		3·7 - 4·1
Palm wax,		1·7 - 1·8
Carnauba wax,		0·76- 0·87
Japan wax,		14·93-15·3
Stearine,		1·1
Rosin,		150·3
Stearic acid,		65·8
Giving normal results by Hübl's method.	I. Mixture of stearic acid, stearine, and ceresin,	21·4
	II. ,, ,, ,, Japan wax, and ceresin,	17·8
	III. ,, ,, ,, stearine, rosin, and ceresin,	22·0
	Commercial beeswax,	14·74
	Mixture of beeswax + 25 per cent. of Mixture I.,	8·42
	,, ,, + 50 ,, ,, ,,	11·3

Kissling[1] gives the following formula for calculating the approximate proportion of beeswax in a mixture of that substance with stearic acid, tallow, Japan wax, and ceresin :—

$$A = 3{\cdot}8\,x + 21{\cdot}4\,(1 - x).$$

Where A represents the acid value determined by Buchner's method, x the required quantity of beeswax, 3·8 the average acid value of pure beeswax, and 21·4 that of a mixture.

Iodine Value.—Beeswax shows a considerable iodine value, indicating the presence of unsaturated compounds.

The iodine value was found by *Buisine* to vary from 8·3 to 11, whilst *Glode-Guyer*[2] obtained an average result of 8·5 in the examination of a number of samples of English wax.

Dieterich's[3] results are in agreement with these, the iodine values of pure yellow wax examined by him ranging from 8·8 to 10·7, whilst white wax gave figures varying from 4·2 to 4·4.

In the case of mixtures, the iodine value is lowered by the presence of paraffin wax or ceresin, raised by stearic acid, tallow, and rosin, but is not changed by the addition of carnauba wax or Japan wax.

The range in the iodine value of normal wax is too great for this test to be of much value, especially in the case of bleached wax, in which it is reduced during the process of bleaching by about 50 per cent.

Acetyl Value.—*Lewkowitsch* found beeswax to have an acetyl value of 15·24, whilst other solid waxes gave the following values :—Carnauba wax, 55·24 ; wool wax, 23·3 ; spermaceti, 2·63 ; and wool wax alcohols, 140·3.

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[1] *Chem. Zeit.*, 1895, xix., 1682.

[2] *Pharm. J.*, 1897, lviii., 308.

[3] *Chem. Zeit.*, 1898, xxii., 729.

The Examination of Beeswax for Special Adulterants.[1]

Detection of Glycerides.—The presence of glycerides (tallow) may be indicated by an increased iodine value, though in the case of Japan wax this test would be valueless.

The ratio of the acid value to the ester value (Hübl's ratio) will also often afford evidence of their presence, though mixtures can readily be prepared giving the normal values of genuine wax (*vide supra*, *Refractometric Examination*).

In *Lewkowitsch's* opinion the determination of glycerol in the products of the saponification of the wax is the most reliable quantitative test.

Buchner's Test for Glycerol.[2]—The saponification residue is evaporated to expel all alcohol, then mixed with water and filtered, and the filtrate tested with potassium bisulphate (formation of acrolein). When considerable quantities of glycerides are present this test can be applied directly to the wax.

Detection of Carnauba Wax.—The presence of carnauba wax in beeswax raises the specific gravity and melting point and lowers the acid value, but does not affect the ester value or saponification value.

When added in any considerable quantity it gives an increased refractometer reading, though the natural variation in beeswax prevents this test from being altogether conclusive.

Allen[3] bases a method of detecting the adulteration upon the fact that the *neutral* portion of the wax yields palmitic acid (m.p. 62° C.) on saponification, whereas carnauba wax yields cerotic acid melting at 79° C. *Lewkowitsch*,[4] however, has shown that this method cannot be of much service seeing that a mixture of these fatty acids may have a melting point lower than that of pure palmitic acid. This is clearly shown in the following table of results obtained by *Lewkowitsch* with mixtures of pure palmitic and cerotic acids :—

Palmitic Acid.	Cerotic Acid.	Melting Point.
Per cent.	Per cent.	° C.
100	0	60
90	10	56·0
85	15	56·5
75	25	60·0
60	40	65·5
50	50	68·6
40	60	70·0
0	100	78·5

An addition of carnauba wax may be indicated by the wax not dissolving completely in chloroform.

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[1] See also *J. Soc. Chem. Ind.*, 1892, xi., 756.

[2] *Chem. Zeit.*, 1901, xxv., 21.

[3] *Commercial Organic Analysis*, 1899, ii., [1], 31.

[4] *Oils, Fats, and Waxes.*

Detection of Wool Wax.—This is the name given to a wax-like residue obtained in the manufacture of wool fat, which being cheaper than beeswax is probably used as an adulterant (see *Wool Fat*). It has an iodine value of 7·8 to 14·2 (*Dieterich*) and, unlike yellow beeswax, is not completely soluble in chloroform.

Buchner recommends the cholesterol test for the detection of *wool fat*, and the same test would also serve for the detection of this product.

Detection of Stearic Acid.—Stearic acid, if added in any quantity, is detected by the increased acid value, and by the melting point and general characters of the acids ultimately obtained from the soap formed on shaking the wax with hot alcohol, and titrating with standard alkali and phenol-phthalein.

Fehling's Test.—This is based upon the solubility of stearic acid in strong cold alcohol as compared with that of cerotic acid. One gramme of the wax is boiled for a few minutes with 10 c.c. of 80 per cent. alcohol, the liquid filtered when cool, and the filtrate mixed with water. In the absence of stearic acid the liquid will remain clear or opalescent, since the cerotic acid separated out from the alcoholic solution on cooling, whilst the presence of stearic acid will be indicated by a turbidity and separation of particles of the acid. This reaction will detect as little as 1 per cent. of stearic acid. The presence of resins will also be shown in this test by the filtrate forming an emulsion when diluted with water.

Buchner[1] recommends the following modification of Fehling's test:—Three grammes of the wax are boiled for a few minutes with 10 c.c. of 80 per cent. alcohol, and the tube then immersed in cold water and shaken until its contents form a thick paste. After standing for an hour the mass is poured on to a filter, and the filtrate mixed with a large excess of water, or with an alcoholic solution of lead acetate or calcium chloride which renders the test more sensitive. Only a faint opalescence is given by normal waxes, though after some hours there is often an amorphous deposit, especially in the case of soft African waxes.

In Buchner's opinion a wax which shows no deposits within two hours may be regarded as free from stearic acid.

Detection of Paraffin and Ceresin.—*Weinwurm*[2] bases a test for paraffin or ceresin on the fact that these substances (and rosin in the proportion of 5 per cent.) are insoluble in an aqueous solution of glycerol, whilst the normal unsaponifiable matter in beeswax is readily dissolved.

Five grammes of the filtered wax are saponified with 25 c.c. of semi-normal alcoholic alkali, the alcohol evaporated, and, after the addition of about 20 c.c. of glycerol, the flask is heated on the water-bath until a clear solution through which printed matter can be read is obtained. On now adding 100 c.c. of boiling water the liquid remains clear and transparent in the case of pure beeswax, but when 5 per cent. of ceresin or rosin is present the liquid becomes turbid. A wax containing less

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[1] *Chem. Zeit.*, 1901, xxv., 21.

[2] *Ibid.*, 1897, xxi., 519.

than 5 per cent. of ceresin may give a clear solution. A second determination is, therefore, made with the same wax after the addition of 5 per cent. of ceresin, and if the solution is only slightly turbid no ceresin was originally present, whilst a marked precipitate points to the presence of about 3 per cent.

In order to determine whether a turbidity in the first test was due to ceresin or rosin, a fresh test is made after the addition of 3 per cent. of ceresin to the wax before saponification. If the original impurity was ceresin there is now a precipitate ; if not, there is still only a turbidity.

Henriques[1] speaks in favourable terms of Weinwurm's process, for which he suggests a slight modification. The test is also recommended by *Buchner*.[2]

Buisine's Method.—*A.* and *P. Buisine*[3] have based a method for the examination of beeswax on the reaction first utilised by *Hell*, according to which alcohols, such as cerylic or cetylic alcohol, yield hydrogen when heated with soda-lime—*e.g.* :—

$$\underset{\text{Cetylic Alcohol.}}{C_{16}H_{33}\,.\,OH} + NaOH = \underset{\text{Sodium Palmitate.}}{C_{16}H_{31}O_2Na} + 2H_2.$$

From 2 to 10 grammes of the wax are melted and mixed with the same weight of powdered potassium hydroxide. The solid mass obtained, on cooling, is powdered and thoroughly mixed with potash-lime in the proportion of three parts to each part of the wax.

The mixture is placed in a tube, which it should nearly fill, and the tube fixed in an iron-bath, filled with mercury and closed by a clamped-down cover provided with three openings. Through the centre opening passes a tube connected with the glass tube and conveying the hydrogen to the eudiometer. The second opening receives a thermometer, whilst the third is for a long iron tube to condense or conduct away the mercury vapour. On heating the mercury-bath to 180° C. the reaction commences, and the temperature is then raised to 250° C. It should not be allowed to rise higher, since hydrogen might be liberated by the action of the alkali on any oleic acid present.

When the reaction is complete the gas is allowed to cool, and its volume measured and calculated at a pressure of 760 mm. and a temperature of 0° C.

The number of c.c. of gas obtained from 1 gramme of wax, multiplied by the factor 0·984, gives the amount of myricylic alcohol.

If the proportion of myricylic alcohol is not required, the hydrogen evolved need not be measured. The residue from the reaction is pulverised and extracted with petroleum spirit in a Soxhlet apparatus. The residue left on evaporation of the solvent is dried and weighed, and the amount of hydrocarbons can be calculated from the result. The proportion of hydrocarbons in genuine beeswax has been found

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[1] *Analyst*, 1897, xxii., 292.

[2] *Chem. Zeit.*, 1901, xxv., 21.

[3] *Mon. Scientif.*, 1890, 1127.

by various observers to range from 12 to 17 per cent., so that this method will detect an addition of about 5 per cent. of foreign hydrocarbons.

Detection of Resins.—Rosin (colophony) raises the specific gravity, acid value, saponification value, iodine value, and refractive index of beeswax, but lowers the ester value.

Donath's Test.—Röttger[1] states that as little as 1 per cent. of rosin may be detected by the following modification of this test:—Five grammes of the wax are boiled for *one minute* with 20 to 25 grammes of nitric acid (sp. gr. 1·32 to 1·33), and the mixture diluted with the same volume of water, and rendered alkaline with ammonia. In the case of pure wax, the liquid separated from the solidified wax will be yellow, whilst wax adulterated with rosin yields a reddish-brown liquid.

By boiling the wax with fifteen parts of 50 per cent. alcohol, filtering the cold solution, and applying the test to the extract, the test is rendered more sensitive, and by weighing the residue left on evaporation of the alcoholic extract, quantitative results may be obtained.

Twitchell's Method.—The method devised by *Twitchell* (Chap. XXII.) for the determination of resin acids in soap can be applied in the case of beeswax after saponification, extraction of unsaponifiable matters by means of petroleum spirit, and liberation of the fatty and resin acids.

CHINESE INSECT WAX.

Recorded Values.[2]

Chinese Insect Wax.

Specific gravity at $\frac{99^\circ \text{C.}}{15{\cdot}5^\circ \text{C.}}$,	0·809-0·811
Melting point,	81°-83° C.
Solidification point,	80°-81° C.
Saponification value,	63

This wax is excreted by an insect, *Coccus ceriferus*, upon the twigs of the Chinese ash, *Fraxinus chinensis*.

It has been known in China since the thirteenth century. Towards the end of August the twigs are cut off and boiled with water, and the wax rising to the surface melted and poured into deep pans.

It is a crystalline substance of a yellowish-white colour, and resembles spermaceti in many respects. It consists chiefly of ceryl cerotate, $C_{27}H_{55} \cdot C_{27}H_{53}O_2$, with slight traces of other esters.

In China and Japan it is used in the manufacture of candles and as a substitute for beeswax.

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[1] *J. Soc. Chem. Ind.*, 1891, x., 575.

[2] Allen, *Commercial Organic Analysis*, ii., [1], 96.

According to a United States Consular Report[1] both the demand for and supply of the wax have shown a marked decrease since the introduction of kerosene oil into China.

SPERMACETI.

Recorded Values.

Spermaceti.

Specific Gravity.	Acid Value.	Saponification Value.	Melting Point.	Solidification Point.	Acetyl Value.	Alcohols.	Authority.
°C.			°C.	°C.		Per cent	
0·8358 at $\frac{60^\circ}{15{\cdot}5^\circ}$	...	128	43-49	43-48	...	51·5	Allen.[2]
0·8086-0·812 at $\frac{99^\circ}{15{\cdot}5^\circ}$	...	...	...	...	...	...	,,
0·905-0·945 at 15°	0-5·17	125·8-134·6	42 47	...	...	...	Kebler.
0·942	...	127·6	44	...	...	...	,, (*a*)
...	2·8	130·6-134·4(*b*)	...	...	...	...	Henriques.
...	...	122·7	...	...	2·63	...	Lewkowitsch.

(*a*) Twice recrystallised from alcohol. (*b*) By cold saponification method.

Source.—The true origin of spermaceti (formerly regarded as whale-spawn, *Sperma ceti*) appears to have been unknown, long after it had come into some degree of use for the preparation of unguents. Its employment for candle-making, like that of whale oils for burning in lamps, seems practically to date from somewhat upwards of a century ago when the whale fishery began to be extensively pursued for commercial purposes.

Even at the present day, however, considerable misapprehension appears to exist both as to the species of cetacea yielding it and the part of the body from which it is derived. Whilst the best known source is the "head matter" of the *Physeter macrocephalus* (p. 388), which largely consists of solid crystallised spermaceti when taken from the dead carcase, considerable quantities are also obtainable from the blubber oil of the same cetacean. During winter this oil solidifies to such an extent, by deposition of spermaceti, that it requires to be steamed to enable it to be removed from the casks. Moreover, analogous if not identical solid deposits form on similarly chilling for lengthened periods the blubber oils of various other species (*vide* p. 389).

Preparation.—The semi-solid oils containing scales of spermaceti will not bear any great degree of pressure during filtration to separate the solid matter, as this very readily passes through even the most

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[1] *J. Soc. Chem. Ind.*, 1897, xvi., 685.

[2] *Commercial Organic Analysis*, ii., [1], 120.

impervious filter cloths. Accordingly the first operation consists in "bagging"—*i.e.*, the material is placed inside long bags of hair or canvas where a separation between the solid and liquid constituents is effected by gravitation alone. The "bagged sperm" in the form of a soft flaky mass, is then transferred to square bags. A pile of bags and boards is formed in successive alternate layers, and by placing weights (at first small but subsequently greater) on the top of the pile, most of the remaining fluid oil is gradually expressed until the mass is sufficiently firm to bear hydraulic cold pressure carried out in presses closely akin to those used for stearine.

After cold pressing, the sperm cake is re-melted, granulated, and pressed several times over at gradually increasing pressures and temperatures so as to remove the last portions of fluid oil, a refining treatment with potassium hydroxide (p. 347) being employed between the last pressings so as to remove not only the last traces of colouring matter, but also free fatty acids formed by hydrolysis. Finally, a glistening white mass is obtained, melting at about 45° C.,[1] and having a specific gravity of about 0·810 at 99° C.

The pressings from these various operations are methodically worked up, in such fashion as ultimately to obtain a second quality of spermaceti of somewhat lower melting point. The potash foots obtained during refining yield on acidification with a mineral acid a mixture of impure spermaceti and palmitic acid; when this is worked up with the other runnings a considerable amount of free fatty acids is contained in the ultimate product, 30 per cent. and upwards of such free acids (essentially palmitic acid) being sometimes present in spermaceti of this lower grade.

Composition.—Spermaceti consists, in the main, of cetin or cetyl palmitate ($C_{16}H_{31}O . C_{16}H_{33}O$), with traces of other similar esters and of glycerides, which can be removed by crystallising the wax from alcohol.

When pure, it contains no free acids, and is devoid of unsaturated compounds, so that it absorbs no iodine. Commercial samples, however, have frequently small iodine values (3 to 4), which, in Lewkowitsch's opinion, is to be attributed to the presence of a small amount of adhering sperm oil.

Adulteration.—Spermaceti is sometimes adulterated with free stearic and palmitic acids (not derived from the foots, as above described), hard pressed glycerides (pressed tallow), and animal waxes and paraffin wax. These latter additions raise the saponification equivalent, whilst free fatty acids and glycerides lower it. The detection of these adulterants is effected in ways substantially the same as those above-mentioned with respect to beeswax.

In Kebler's opinion[2] adulteration is best detected by determining

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[1] According to Field (*J. Soc. Arts*, xxxi., 840), the spermaceti extracted from the blubber oils of the true bottlenose whale (*Balæna rostrata*) has a slightly higher melting point than that from the sperm whale or cachalot (*Physeter macrocephalus*).

[2] *Amer. J. Pharm.*, 1896, lxxviii., 7.

the acid and saponification values; and he points out that it is not easy to add any considerable quantity of a foreign substance without interfering with the characteristic crystalline structure of spermaceti.

WOOL FAT.

WOLLFETT.

Recorded Values.

Wool Fat.

Specific Gravity.	Saponification Value.	Iodine Value.	Hehner Value.	Melting Point.	Unsaponifiable Matter.	Fatty Acids.	Authority.
				°C.	Per cent.	Per cent.	
0·970 at 15°C.,	82-130	17-27	60	39-42	...	...	Holde.
0·973 ,,	...	...	...	...	...	...	Schädler.
...	...	23-52	...	...	38·7-43·9	...	Herbig.
...	...	17·1-28·9	...	...	43·6	59·8	Lewkowitsch.

Fatty Acids.

Melting Point.	Solidification Point.	Iodine Value.	Authority.
°C. 41·8	°C. 0·0	17	Lewkowitsch.

The properties and application of the fat obtained from the wool of sheep and hair of goats have long been known; and a description of its preparation and uses was given by *Pliny* in his natural history.

The general methods of extraction have already been described on p. 322.

According to *Rosengren*,[1] extraction of the fat by washing the wool with water gives a product containing about 35 per cent. of saponifiable fatty acids, whilst the substance obtained by extraction with solvents contains 12 per cent. of saponifiable fatty acids. The fat extracted with solvents is inferior in quality, since it contains a considerable amount of resin-like substances.

A sample of "Yorkshire grease" examined by *Lewkowitsch* had the following composition:—Volatile fatty acids, 1·28; insoluble fatty acids, 20·22; combined fatty acids, 48·47; and alcohols, 36·47 per cent.

Composition.—Wool fat is a complex substance which is much more akin to the waxes than to the fats, since it contains a much

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[1] *Chem. Zeit.*, 1899, xxiii., 382.

larger proportion of esters of higher alcohols than of glycerides. Among the fatty acids that have been described as constituents are :—Acetic, butyric, iso-valeric, caproic, myristic, palmitic, stearic, carnaubic, cerotic, lano-palmitic and lanoceric acids, together with certain acids of unknown composition.

The alcohols described include lanolinic alcohol, carnaubylic alcohol, cerylic alcohol, cholesterol, isocholesterol, and numerous other compounds of yet undetermined composition.[1]

Lactonic compounds have also been isolated by *Darmstaedter* and *Lifschütz.*

Schulze [2] has found that different specimens of wool fat vary greatly as regards the amount of cholesterol, and in the ratio between the proportion of alcohol and of acids.

The *lano-palmitic* acid, separated by *Darmstaedter* from the portion of the saponified fat dissolving in alcohol,[1] had the composition $C_{16}H_{32}O_2$, and melted at 87° to 88° C.

Unsaponifiable Matter.—*Lewkowitsch* [3] obtained 51·84 per cent. of unsaponifiable matter from the neutral part of the fat. This melted at 46° to 48° C., had an iodine value of 26·35, and showed an increase of weight of 8·26 per cent. on acetylation. From the low iodine value he concluded that cholesterol and iso-cholesterol could not have been present in very great proportion.

Herbig [4] determines the unsaponifiable matter by saponifying the fat under pressure, as first proposed by *Lewkowitsch*, precipitating the fatty acids with calcium chloride at a temperature of 70° to 75° C., extracting the calcium salts with freshly distilled acetone, washing the residue into a weighed basin with ether, and drying it at 105° C.

In this way the following results were obtained with wool fats of different origin :—New Zealand, 43·66 to 43·94 ; Russian, 38·72 to 39 ; South American, 48·31 to 48·5.

Properties.—Wool fat is a dirty yellowish-brown substance with an unpleasant smell.

It is miscible with water in all proportions, a property which adds to its value as an emollient.

Saponification Value.—It is a difficult matter to effect the complete saponification of wool fat. Neither hot saponification by boiling with alcoholic potassium hydroxide, nor cold saponification by Henriques' method are sufficient.

Lewkowitsch,[5] however, has shown that good results are obtained by carrying out the saponification under pressure, and his results have been confirmed by *Herbig*.[6]

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[1] Darmstaedter and Lifschütz, *Ber. d. d. chem. Ges.*, 1897, xxvii., 2890; xxi., 97.

[2] *Ber. d. d. chem. Ges.*, 1898, xxxi., 1200.

[3] *J. Soc. Chem. Ind.*, 1896, xv., 14.

[4] *Dingler's polyt. J.*, 1896, ccxcvii., 135, 160.

[5] *J. Soc. Chem. Ind.*, 1892, xi., 134.

[6] *Ibid.*, 1894, xiii., 1068 ; 1896, xv., 138.

Lanoline.

Under the name of lanoline, purified wool fat, *adeps lanæ*, etc., there is sold a purified form of wool-fat from which the free fatty acids and ash have been to a large extent removed.

Kleinschmidt[1] found three commercial samples of purified wool fat to have the following composition:—

	Agnine.	Lanolin Puriss.	Lanoline.
Specific gravity,	0·94	0·85	0·86
	Per cent.	Per cent.	Per cent.
Water,	0	19·26	23·74
Free fatty acids (as stearic acid)	22·12	7·75	1·25
Mineral matter,	0·08	0·17	trace
Esters—Solid alcohols,	73·46	41·9	53·7
Volatile fatty acids (as caproic acid),	0·44	1·6	1·48
Insoluble fatty acids,	27·6	36·12	23·7

A sample examined by *Paessler*[1] contained the following constituents:—Water, 0·10; ash, 0·03; solids not fat, 0·61; readily saponifiable fat, 38·80; fat saponified with difficulty, 4·06; and unsaponifiable matter, 56·40 per cent.

Recorded Values of Lanoline.

Specific Gravity.	Melting Point.		Saponification Value.	Iodine Value.		Acetyl Value.	Solidification Point of Fatty Acids.	Melting Point of Alcohols.	Acid Value.	Authority.
	Fat.	Fatty Acids.		Fat.	Fatty Acids					
	°C.	°C.					°C.	°C.		
0·973	36 to 42·5	41·8	98·3 to 102·4	10·6 to 28·9	17	108·7 to 122·5	40·0	33·5	...	Donath.
...	40	...	81·4	30·9	...	...	...	...	2·8	Paessler.
...	...	...	82·9 to 89·9	...	...	...	...	...	0·67 to 1·81	Herbig.
...	38-42	...	80·8 to 82·9 (*a*)	...	...	...	...	...	0·6 to 1·8	Cochenhausen.

(*a*) Readily saponifiable esters.

Properties and Tests of Purity.—Lanoline is a white or yellowish-white semi-solid mass; it is readily soluble in chloroform, ether, carbon bisulphide, and acetone, but is less soluble in alcohol. It does not readily become rancid, and is, therefore, particularly suitable for cosmetic or medicinal preparations.

It should be free from soaps, glycerides, chlorine, metallic impurities, and salts.

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[1] *Das Wollfett*, 1901, 92.

Lifschütz[1] gives the following criteria of a well-purified lanoline :—(1) It should be soft and pliable, and remain so after exposure to the air, and should also be free from any odour of crude fat. (2) It should not become darker on heating. (3) On boiling 0·5 gramme with 5 c.c. of glacial acetic acid only a brownish-yellow tint should be produced, and there should be no green coloration on adding four or five drops of sulphuric acid to the liquid. (4) Not more than two drops of decinormal alkali should be required for the neutralisation of 5 grammes. (5) It should be free from ash. (6) It should be free from chlorine, which is tested for by boiling the fat with absolute alcohol and a drop of nitric acid and adding silver nitrate to the filtrate.

Another test for distinguishing between crude wool fat and lanoline is to pass a current of steam for thirty minutes into hot water, on the top of which is a melted layer of the fat. In the case of an imperfectly purified product the lower aqueous layer forms a white milky emulsion which does not separate for a long time (*Lifschütz*[2]).

For the detection of foreign fats recourse must be had to the determination of the different chemical constants, especially of the fatty acids, and to a quantitative determination of glycerol.

Other Wool-Fat Products.

Distilled Wool Fat.—On distilling wool fat in a current of superheated steam, the distillate consists mainly of free fatty acids, together with cholesterol and its esters and hydrocarbons.

Distilled wool fat is a yellow or brownish mass, which can be separated by crystallisation into a solid and a liquid portion.

The following results were obtained by *von Hübl* in the examination of a commercial sample :—Melting point, 42·1° C.; solidification point, 40·0° C.; saponification value, 169·8; iodine value, 36·0; melting point of fatty acids, 41·8° C.; solidification point of fatty acids, 40·0° C.

Wool Wax.—The name "wool wax" is applied by *Lewkowitsch* to the neutral portion of wool fat. It has also been used to describe commercial products consisting of the more solid portions separated by treatment of the crude fat with various solvents.

Thus *Jaffé* and *Darmstaedter* (Eng. Pat. 14,114, 1892) treat the wool fat with fusel oil, chill the solution below the melting point of the fat, and separate the harder portion (wool wax) that deposits.

Maertens (Eng. Pat. 9,503, 1895) fractionates wool fat into several products by treating it with acetone and alcohol. Of these the three main fractions are :—(1) A transparent semi-fluid mass consisting of free fatty acids, esters, and resin-like substances. This is soluble in cold alcohol and cold acetone. (2) An oily opaque liquid or semi-solid, soluble in cold acetone, but insoluble in cold alcohol. This consists, in the main, of esters of cholesterol, etc. (3) An opaque wax-like solid of a white or reddish colour, which is insoluble, or nearly so,

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[1] *Chem. Zeit.*, 1898, xxii., [Rep.], 119.

[2] *Chem. Centralbl.*, 1898, i., 1002.

in cold alcohol or acetone, but dissolves in thirty times its volume of boiling acetone. This consists of a mixture of esters of cholesterol, etc.

Wool Fat Lubricants.[1]—The refuse fatty acids, etc., left in the purifiers in the manufacture of lanoline are incorporated with petroleum at 120° to 200° C., then treated with sufficient alkali to neutralise half the free acids, and the water expelled by heat. In this way a lubricant is obtained which retains soap in solution without the presence of water.

Wool fat lubricants are said to have given good results in practice. They are unaffected by heat or cold, and have from five to eight times the viscosity of solid lubricants containing soaps.

Wool Fat Substitutes.—*Axelrad*[2] describes a method of preparing lanoline substitutes by saponifying spermaceti with alcoholic alkali, treating the soap solution with calcium chloride, drying the calcium soap and distilling it at 340° C. Lanoline substitutes may also be made by mixing suitable proportions of a petroleum base with cetyl alcohol and water, and preferably about 5 per cent. of lanoline to give the texture of wool fat.

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[1] Rosengren (*loc. cit.*).

[2] *J. Ind. Eng. Chem.*, 1917, ix., 1123.

§ 6. The Candle Industry.

CHAPTER XVII.

MATERIALS USED IN CANDLE-MAKING.

ORIGIN OF CANDLES.

In all probability the earliest forms of illuminating agents of the nature of *candles* (*i.e.*, containing something serving the purpose of wick surrounded by more or less solid adherent combustible matter) were simple links or flambeaux consisting of fibrous vegetable stalks, etc., soaked in natural bitumen or asphalt, vegetable resin, or animal fatty matter; these being obvious developments of the yet simpler primeval torches consisting of splinters of pine and similar woods, either naturally containing or smeared with resinous matter.

Lamps, or reservoirs of fluid oil furnished with a wick for burning, seem to have been invented at a very early period of the world's history, and to have speedily superseded the primeval resinous wooden torch for general household purposes amongst the earlier civilised nations, although for outdoor illuminations, and especially amongst the Scandinavians and other northern tribes, pine splinter torches and similar rude contrivances of the flambeau character were still chiefly used.

Rushlights, in which the pith of rushes served as wick and the combustible matter was tallow or other animal fat applied by dipping the pith in melted grease, and superior forms in which wax was used instead of tallow, moulded by hand round the rush whilst rendered plastic by means of warmth,[1] appear to have been in considerable use amongst the Romans, hempen or flaxen unspun wicks taking the place of rush pith in the better kinds of wax lights. Thus in Herculaneum the remains of a chandler's establishment have been unearthed, whilst numerous passages in various Latin authors indicate that the torch (*tæda*), the lamp (*lucerna*), the tallow candle or rushlight (*sebaceus*), and the wax light (*cereus*) were all in use in the early centuries of the Christian era,[2] the oil lamp being still the most extensively used illuminant amongst the well-to-do classes, wax lights ranking next.

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[1] Such a candle, believed to date from the first century, is in the British Museum.

[2] *Vide* Leopold Field, "Cantor Lectures," *J. Soc. Arts*, xxxii., 821, *et seq.*

With the exception that wax tapers were largely used for ecclesiastical purposes, as well as private illumination. during the middle ages, and that some improvements were consequently introduced as regards their general size and finish, little advance in the art of candle-making seems to have been brought about until the fifteenth century, when the process of "moulding" was introduced by the Sieur de Brez; but the manufacture of rushlights and of "dip" tallow candles, as well as of waxen tapers, had by that time become a trade in itself, having to a considerable extent passed out of the region of ordinary household operations carried on by each family for the supply of its own wants, and into the hands of special candle-makers (*candelarii*, or chandlers), who made tallow and other candles for sale to the general public, at any rate in the larger towns. In country districts, however, rushlights and tallow candles, of more or less rough home-made manufacture, still continued to be the only available means of artificial illumination other than oil lamps, for the great majority of the population; a state of matters, indeed, not entirely obsolete even at the present day in some highly rural localities. In some savage countries highly oleiferous nuts, strung together on a fibrous twig, are burnt like candles; as one is consumed the next one becomes lighted and burns till exhausted.

Combustible Materials.—At the present time the combustible matters (in addition to the wicks) used for candle-making may be divided into four classes, viz.:—(1) Those natural glycerides which are sufficiently solid at ordinary temperatures to admit of being used for the purpose, or which yield sufficiently solid glycerides by pressure; more especially tallow and similar animal fats, together with vegetable products of corresponding consistency, such as coconut stearine, piney tallow, and solid fats of *Stillingia*, *Bassia*, and other genera. (2) Hydrogenated oils and the fatty acids derived from them. (3) Substances of waxy character, such as beeswax and the vegetable waxes, essentially consisting of non-glyceridic compound ethers; also including spermaceti. (4) Free fatty acids of sufficiently high melting point, obtained from natural oils and fats by saponification processes, and mechanical separation of more fluid ingredients. (5) Paraffin wax and analogous hydrocarbons of mineral origin, or formed by destructive distillation. Of these the substances of the latter two classes are those most largely used, more especially the last, in this country, although "stearine" candles are somewhat preferred on the Continent. The trade in wax and spermaceti candles is comparatively small, although by no means insignificant in actual amount; whilst the use of unsaponified glycerides, whether as tallow "dip" candles, consisting of such glycerides only, or as "composite" mixtures of glycerides and free fatty acids, is steadily diminishing in favour of the other kinds of illuminants, although far from being extinct, especially in the case of night-lights, which are largely made of coconut stearine.

In the manufacture of tallow dip candles no special preparation of the tallow for use is necessary further than the rendering and purifying processes already described (Chaps. X. and XI.); the harder varieties are usually preferred, although if too hard there is more risk of cracking. In the case of beeswax, air- and light-bleached wax (p. 353) is employed in preference to that bleached by chemical processes, especially such as involve the use of chlorine; for, irrespective of a greater tendency to become yellowish on keeping, such chemically bleached waxes are apt to possess a crystalline grain which spoils the appearance of the candle, and when bleached by chlorine, to give off fumes of hydrochloric acid when burnt, owing to the formation of chloro-substitution compounds during the bleaching process. Paraffin wax and the analogous waxy hydrocarbons obtained from ozokerite, etc., require no treatment for candle-making other than the pressing and purifying processes gone through during their manufacture for the purpose of raising the melting point to the required extent. The isolation of solid free fatty acids from natural glycerides, however, is a somewhat complex operation capable of being carried out in several ways.

MANUFACTURE OF "STEARINE."

The numerous processes proposed, and more or less actually used on a manufacturing scale for the isolation of solid fatty acids from appropriate glycerides, may be classified under the following heads:—

1. Processes in which the glycerides are saponified by alkalis, alkaline earths (such as lime), or other suitable basic materials, by boiling under ordinary pressure; to effect which operation a more or less considerable excess of base is usually found necessary in order to complete the saponification.

2. Processes analogous to the preceding, except that the operation is carried out at a somewhat higher temperature obtained under increased pressure; excess of base is in this case unnecessary, for, in general, practically complete saponification and hydrolysis can be thus easily brought about even when considerably less base is present than is chemically equivalent to the fatty acids formed, and although the temperature does not rise sufficiently high to decompose any considerable fraction of the glycerol set free.

3. Processes in which hydrolysis is effected under the influence of acids, especially sulphuric acid; in this case the liberated acids are usually distilled by the aid of superheated steam, so as to separate them from non-volatile pitchy matters formed as by-products; in Bock's process (*infra*) this distillation is unnecessary. More or less glycerol is usually destroyed by the action of the acid. To this group also belong Twitchell's and analogous processes.

4. Processes in which hydrolysis is brought about under the influence of water alone (under great pressure, or as highly superheated steam). In these processes the glycerol is often largely destroyed by the heat (sometimes completely so), a much higher temperature being required than in the case of methods of the second class.

5. Processes in which hydrolysis is effected by means of the enzymes contained in oil-seeds, and especially castor-oil seeds.

The Chevreul-Milly Process—Alkaline Saponification Process in Open Pans under Ordinary Pressure.—The first attempts to utilise solid free fatty acids for candle material, were made about 1825 by Chevreul and Gay Lussac, employing alkalis (potash and soda) to effect the saponification of tallow. For a variety of reasons, this process proved to be commercially a failure; but a few years later, by substituting lime for alkalis and otherwise employing more suitable arrangements, de Milly succeeded in making the manufacture of "stearine" candles from tallow a sufficiently remunerative undertaking to render it a practical industry.

As carried out at the present day, the process differs little in essential points from what it was more than half a century ago, the chief differences lying in the scale on which the operations are effected, and the frequent use of mixtures of vegetable and other substances with tallow (*e.g.*, a mixture of palm oil and tallow or other suitable fatty matters or hydrogenated oils) instead of tallow only, with the result that a better quality of mixed fatty acids is usually obtained—*i.e.*, a mixture which allows the solid acids to crystallise and "granulate" more readily, so as to be more easily pressed for the separation of liquid acids.

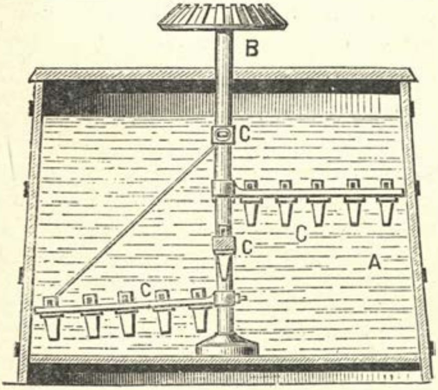

Fig. 108.—Open Pan used in Manufacturing Stearine.

The fatty substances being generally purchased in casks, a steam jet is applied at the bunghole, and the fats melted out in a tank, whence they are pumped or run by gravitation into the decomposing pan, usually constructed of wooden staves (preferably of oak) strongly bound together, and forming a large tub or tun, sometimes lined with sheet lead.

This is provided with a stirring arrangement, consisting of a central vertical shaft with arms carrying paddles and rakes so as to intermix the contents thoroughly (Fig. 108). Quicklime, in the proportion of 12 to 15 pounds per 100 of fat, is mixed with water to a cream and run into the tun, the mass heated up by steam blown in through a perforated horizontal coil at the bottom of the tub, or a series of jets distributed over the bottom, and the whole kept agitated for some hours, a cover being placed over the tub to prevent loss by splashing, while steam is being blown through gently so as to keep the whole boiling.[1] Glycerol is thus set free, and a mixture of lime-salts formed (chiefly stearate, palmitate, and oleate), practically insoluble in water, and solidifying on cooling to a hard mass known as "rock." The aqueous glycerol solution or "sweet water" is run off and utilised for glycerol extraction.

To isolate the fatty acids, the rock is boiled up in a lead-lined vat with steam, diluted sulphuric acid being added in slight excess of the quantity required to saturate all the lime present.[2] Sulphate of calcium separates out, whilst the free fatty acids rise to the top; after standing and cooling somewhat, these are skimmed off and boiled up, firstly with highly dilute sulphuric acid to decompose the last traces of lime soap, and then with water, using wet steam, so as thoroughly to wash out all sulphuric acid and admixed mineral matters.

Finally, the fluid fatty acids are transferred to shallow cooling pans, such as the series indicated in Figs. 109 and 110. Here the melted fatty acids are run from a trough, F, through nozzles, D D D, into the uppermost of the pans, C C C, supported by a wooden framework, A A, and iron crossbars, B B. When the pans are filled, the stream of melted matter is shut off by means of the spigot, E. In these cooling pans they solidify to a semi-crystalline mass on cooling and standing; for the purpose of pressing out the fluid acids, this solidification is best allowed to take place in metal dishes, so that the solid cakes formed are obtained in the form of slabs about an inch or three-fourths inch thick, and of such size as to fit into the cake boxes of the hydraulic press used. The temperature during this period should lie between 21° and 32° C. (70° to 90° F.), so that whilst the "seeding" or crystallisation of the solid acids (chiefly stearic and

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[1] Assuming the mixture of fatty substances to have a mean saponification equivalent of 280, the quantity of lime (CaO) theoretically equivalent to the fatty acids formed would be 28 parts per 280, or 10 per cent.; with fatty substances of higher saponification equivalent, proportionately less lime would be required, and *vice versâ*. Some excess of lime, however, is necessary in order to ensure tolerably complete action; moreover, in practice, quicklime is not pure CaO, a little moisture, calcium carbonate, and more or less siliceous and clayey matter being present, all of which are inert so far as effecting saponification is concerned. A first-class quicklime, made from a pure limestone, may contain (when freshly burnt) some 95 per cent. of CaO (exclusive of calcium carbonate); but 85 to 90 per cent. is more nearly the usual average, and less with very poor limes.

[2] For every 56 parts of actual lime, CaO, used, 98 parts of actual sulphuric acid, H_4SO_2, are required; roughly, 2 parts of B.O.V. (brown oil of vitriol) to 1 of quicklime.

palmitic) may take place completely, as little oleic acid as possible may be retained in the body of the crystals formed.

The slabs of " separation cake " finally consist of a spongy mass of granular or crystallised solid acids, with liquid oleic acid (containing solid acids and colouring matters in solution) disseminated through the interstices. By wrapping them in press cloths, and placing them in the cake boxes of a hydraulic press, the brownish liquid acids are gradually squeezed out, and the comparatively colourless solid crystals retained. Instead of directly pressing the granulated cakes, it is often preferable to rasp them into shreds by a machine, and to press the raspings; a more complete expression of liquid acids is thus brought about.

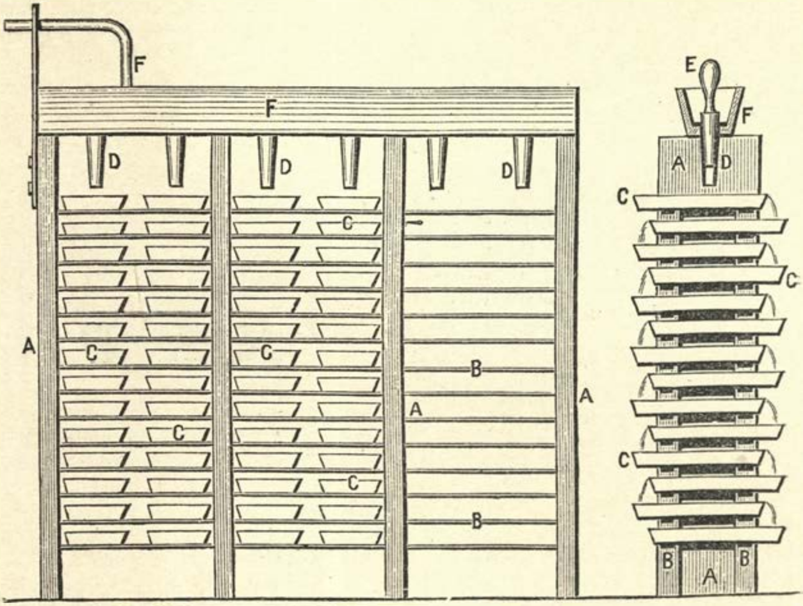

Fig. 109. Fig. 110.

Figs. 109 and 110.—Crystallising Pans.

The residual press cake, however, still retains a certain amount of liquid acids, rendering its melting point too low; to remove these the press cakes are melted by steam, cast afresh into slabs in shallow trays, allowed to stand to granulate at a temperature of about 30° C., rasped to coarse powder, and again pressed in a different machine where the cake boxes are heated by the regulated admission of steam into the plates, in the body of which channels are hollowed out for the purpose.

Fig. 111 represents a form of horizontal hot press thus arranged, steam being admitted to the plates by the pipes, E E. A A A represent the packets of raspings undergoing pressure; B the piston of the hydraulic ram working in the cylinder, C; D the framework; F a chain whereby the plates are drawn asunder for the removal of the cakes when the operation is finished; G water supply pipe to ram-cylinder from accumulator. The temperature of the hot press varies somewhat with the kind of material employed, but is generally not far from 50° C. (122° F.) for stearine of high melting point; for inferior stearine melting more easily, the temperature is proportionately lower.

The hot press cake finally obtained is melted by means of steam with a little water acidulated with sulphuric acid, and then vigorously agitated with the acid fluid for some time for the purpose of removing traces of lime salts still retained; finally the acid liquor is run off, and the residue boiled up several times successively with plain water. The purified mixture of stearic and palmitic acids is then cast into blocks for use in the candle factory. Small quantities of vegetable wax, beeswax, etc., are sometimes added to "break the grain"—*i.e.*, to prevent the formation of visibly large crystals during solidification.

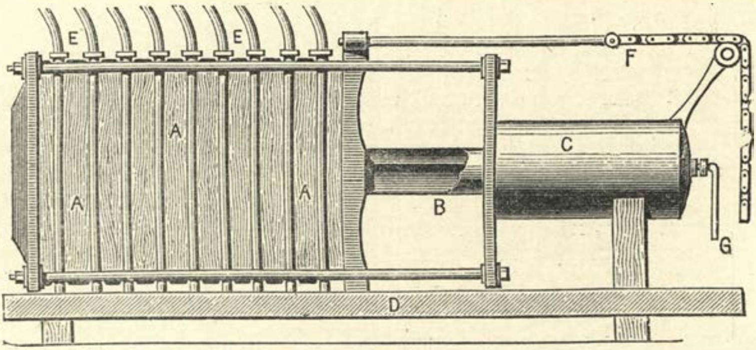

Fig. 111.—Hot Press.

Even when the fatty matters employed are highly rancid and impure, an almost perfectly white "stearine" can be thus manufactured by the lime process. The yield of pure solid hot-pressed acids, however, is materially influenced by the presence and nature of abnormally large proportions of oleine (existing in softer fats, etc.) or other substances (*e.g.*, wool-grease), not only on account of the diminution in amount of solid fat acids present, but also because of the increased amount of these acids removed in the "red oils" (*vide infra*).

Fig. 112 represents a general view of the disposition of the apparatus used in the saponification of fatty matters by the open pan process.[1] A, tub from which lime is emitted. B, lead-lined vats with steam pipes for boiling limes and fats. C, similar decomposing vats where

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[1] L. Field, *J. Soc. Arts*, xxxi., 859.

the rock is boiled with sulphuric acid. D D, rack holding pans for caking mixed acids. E, cold press. F, hydraulic pumps. G, pan for re-melting press cake. H, hot press. I, vat for melting hot-pressed stearine for final washing with water and casting into blocks.

Moinier and Boutigny's Modification.—Moinier and Boutigny modify the Chevreul-Milly process by submitting the melted tallow, etc., to a preliminary treatment with hot water and a current of impure sulphur dioxide (produced by the action of hot sulphuric acid on sawdust, charcoal, etc.). After an hour the lime-cream is added and the whole well agitated, whereby the mass increases in consistence with considerable frothing, by and bye becoming pasty. The sulphur dioxide is then shut off and the rock finished by boiling up with steam, etc., as usual. The yield of fatty acids is stated to be thus increased by some 4 per cent. The hot press cake is finally refined by boiling first with water acidulated with sulphuric acid, then with water alone, white of egg (1 egg per 100 lbs.) being introduced whilst boiling so as to coagulate and remove impurities as in clarifying coffee, etc.

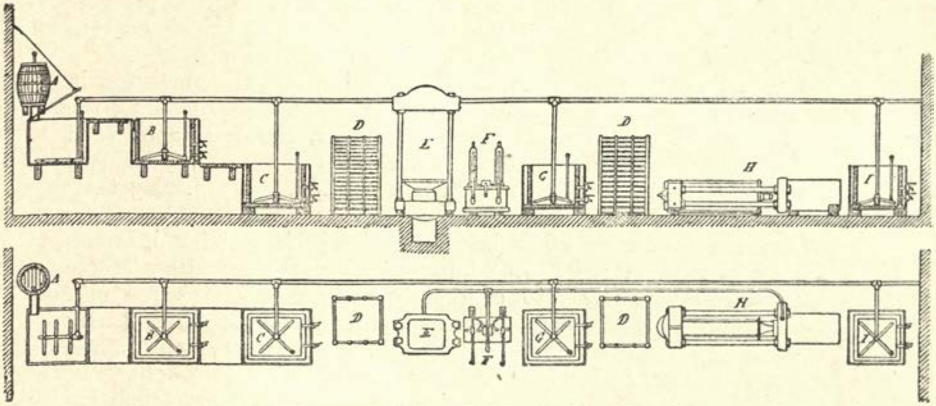

Fig. 112.—Plant for Saponification by Open Pan Process.

Separation of "Red Oils."—On p. 727 are given some analyses of original fatty acid mixture, cold press cake, and hot press cake, etc., illustrating the effect of the process in separating oleic acid from the solid fatty acids, and the increase in melting point thus effected. The hot press grease usually contains enough solid fatty acids to raise its fusing point to at least that of the original mixture of fatty acids before cold pressing; it is generally worked up together with fresh fatty acids by fusing and granulating the mixture in trays for the cold press. The outer edges of the hot press cake retain some amount of more fusible grease, and are therefore usually pared off and worked up with the rest of the hot press grease.

The "red oil" or "oleine" running from the cold press contains a considerable quantity of palmitic and stearic acids in solution, the precise amount depending on the temperature at which the pressing is conducted; on chilling somewhat, more or less solid fatty acids separate, usually in a finely divided form. When it is desired to obtain red oils containing as large a proportion of oleic acid and as little solid acids as possible, the oil is chilled and the resulting somewhat pasty mass passed through a filter press, such as shown in Figs. 68, 71, the greasy solid fatty acids thus obtained being worked up with fresh batches of the original mixture of acids. For the manufacture of oleine soap this treatment is not indispensable, but inasmuch as the solid fatty acids are considerably more valuable than the fluid ones, it is obviously desirable to obtain as large a proportion of the former as possible. For the same reason it is essential that the saponification of the fats used should be as nearly complete as possible, not only because all the stearic and palmitic glycerides that escape saponification are lost so far as solid fatty acids are concerned (being expressed fluid during the pressing operations), but also because their presence tends to prevent the proper crystallisation of the solid acids, and thus to increase the proportion of these contained in the red oils.

In actual practice, it is impossible to carry the decomposition in open pans to absolute completeness without seriously prolonging the operation, which entails extra cost; so that a few per cents. (and sometimes much more, up to 10 or 12 per cent.) of the glycerides used are generally left undecomposed in the rock, ultimately finding their way into the red oils.

When the tallow used has been adulterated by mixing in wool-grease or similar material containing unsaponifiable matters, these substances are generally also ultimately contained in the red oils, thereby diminishing the proportion of "stearine" obtainable, partly because of the smaller proportion of solid glycerides present in the adulterated tallow, and partly because the presence of wool-grease, like that of unsaponified fat, tends to interfere with the crystallisation of the acids, and hence causes the red oils to retain more solid acids.

Moreover, when the red oils are made into soap, a deteriorating effect (for certain purposes) is brought about in the resulting soap; on solution in water and standing, soap containing such unsaponifiable matter is apt to throw up an oily film, rendering the solution liable to spot and grease goods rinsed through the soap solution. Accordingly, it is preferable to buy tallow by analysis, the price varying according to the proportion of solid fatty acids present (estimated by Dalican's process (*q.v.*) or otherwise), and deductions being made for unsaponifiable constituents. As yet, however, this system does not seem to have been widely adopted in this country.

Composition of "Rock."—The following analyses represent the general composition of open pan "rock" as obtained on the manufacturing scale; A being normal rock made from genuine tallow mixed with about one-fourth its weight of palm oil; and B rock from tallow adulterated with wool-grease containing a considerable amount of cholesterol and other unsaponifiable matters:—

	A	B
Lime present as lime soap (CaO),	7·50	6·27
Lime used in excess (CaO),	1·95	2·41
Fatty anhydrides [1] present as lime soap,	73·30	61·20
Unsaponified glycerides,	5·55	8·40
Unsaponifiable organic matter,	2·75	12·00
Water and carbonic acid (CO_2), combined with the excess of lime; sand and grit, etc.; uncombined water (moisture),	8·95	9·72
	100·00	100·00

Since 100 parts of triglycerides of mean molecular weight near 285 represent about 92 parts fatty anhydrides, the fatty anhydrides present in these two samples represent respectively about 80 and 66 parts of original glycerides per 100 of rock; hence the proportion of glycerides originally used which remain unsaponified are (A) $\frac{5{\cdot}55}{80 + 5{\cdot}55} \times 100 = 6{\cdot}5$ per cent., and (B) $\frac{8{\cdot}40}{66 + 8{\cdot}40} \times 100 = 11{\cdot}3$ per cent.—*i.e.*, in the first case about $\frac{1}{16}$, and in the second about $\frac{1}{9}$, of the original glycerides escaped saponification.

Analysis of Rock.—This is conveniently effected by taking a known weight of an average sample and boiling it with water to which an excess of standard acid (preferably hydrochloric) has been added, until completely decomposed. On standing the liberated fatty acids, etc., form a cake on the top, which is carefully removed, dried, and weighed.[2] The free fatty acids it contains are then titrated in alcoholic solution with standard alkali, and the examination for admixed glycerides and unsaponifiable matters proceeded with, as in the case of separation cake (*vide infra*), p. 726 The excess of acid in the aqueous fluid is back titrated, so as to obtain the acid neutralised by the total lime, the amount of which can be calculated from the result; whilst the lime present as lime soap (combined with fatty acids) is similarly calculated from the amount of alkali neutralised by the fatty acids.

For example, 10 grammes of a given sample of rock were boiled with water and 50 c.c. of normal acid; on back titration 16·7 c.c. were found to be unneutralised; hence 33·3 c.c. were neutralised, equivalent to 0·932 CaO = 9·32 per cent. of total lime. The separated fatty acids, etc., weighed 8·215 grammes, and neutralised 25·9 c.c. of normal alkali, equivalent to 0·725 gramme, or 7·25 per cent. of CaO; whence

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[1] "Fatty anhydrides" = fatty acids, less an equivalent of water—*e.g.*, in the case of stearic anhydride, $\left.\begin{matrix}C_{18}H_{35}O\\ C_{18}H_{35}O\end{matrix}\right\}O$; so that the sum of the fatty anhydrides and the lime combined with them as lime soap, represents the actual amount of lime soap present. In the above two instances the amounts of lime soap are (A) 73·30 + 7·50 = 80·35; (B) 61·20 + 6·27 = 67·47.

[2] If the quantity is too small for accurate determination in this way, the liberated fatty acids, etc., may be dissolved by ether, and the ethereal solution separated and evaporated, etc., as in the parallel case of soap analysis (Chap. XXII.).

0·932 − 0·725 = 0·207 gramme of excess of lime was present, or 2·07 per cent.

On further examination, the separated fatty acids were found to contain 0·535 gramme of unsaponified glycerides and 0·235 gramme of unsaponifiable matter. Hence the actual fatty acids present in the 8·215 grammes of cake obtained amount to 8·215 − (0·535 + 0·235) = 7·445 grammes. In order to reckon the fatty anhydrides equivalent to this amount of fatty acids, 18 parts of water must be subtracted for 56 of CaO combined with them as lime soap—*i.e.*, $\frac{18}{56} \times 0{\cdot}725 = 0{\cdot}233$ gramme of water must be subtracted, leaving 7·445 − 0·233 = 7·212 grammes of fatty anhydrides present as lime soap.

Hence the whole analysis is—

Lime present as lime soap (CaO), . .	0·725 grammes	= 7·25 per cent.	
„ in excess, ...	0·207 „	= 2·07 „	
Fatty anhydrides present as lime soap, .	7·212 „	= 72·12 „	
Unsaponified glycerides, ...	0·535 „	= 5·35 „	
Unsaponifiable matter, ...	0·235 „	= 2·35 „	
Combined water, CO_2, sand, moisture, etc. (by difference), ...	1·086 „	= 10·86 „	
	10·000 „	100·00 „	
Total lime soap present, .	7·25 + 72·12 „	= 79·37 „	
Total lime present, .	7·25 + 2·07 „	= 9·32 „	

Milly Autoclave Process—Saponification with Alkalis (Lime) under Increased Pressure.—As practically carried out, this process is virtually a combination of the previous process, and that subsequently devised by *Tilghmanns* in which fats are hydrolysed by the action of water under high pressure.

The tallow and palm oil or other fatty mixture is pumped into a stout copper pressure vessel or *autoclave* (Fig. 113), and lime made into a thin cream with water added in much smaller proportion than in the open pan process, usually 2 to 3 parts of lime per 100 of fat, or somewhere about one-quarter of the theoretical amount instead of an excess. High pressure steam is then gradually blown in from a boiler until the pressure amounts to at least 7 or 8 atmospheres, and preferably 12 to 15, especially when tallow only is used, as in many Continental factories.

After some hours' continuance of digestion under pressure the fat is practically completely saponified and hydrolysed, partly by the lime, partly by the action of water only, the presence of the lime soap formed by the saponification greatly facilitating the hydrolysis; the mixed "sweet water," fatty acids, and lime soap are blown off into a tank, where the latter separate from the aqueous glycerol solution, and are then treated with sulphuric acid precisely as in the open pan process, saving that as much less lime is used, a proportionately smaller quantity of acid is required. The further operations of separating solid fatty acids by pressure, etc., are identical in the two processes.

The remarks above made respecting the objectionable results brought about when any considerable amount of glycerides escapes saponification, and when the tallow is adulterated with wool-grease or other unsaponifiable matters, obviously apply equally in the present case. As regards the former point, the following figures were obtained by the author (*Alder Wright*) in a set of experiments on a manufacturing scale made with the object of determining the effect of increased time in diminishing the amount of unsaponified grease.

A series of charges was worked off in the same autoclave, the mixture of fats (tallow and palm oil), and the proportion of lime used, and the pressure being as nearly as possible the same throughout, but the times being different. The fatty acids obtained (after separation from lime by sulphuric acid) were analysed so as to obtain the data for determining the proportion of grease unsaponified during the digestion. The figures ultimately obtained on averaging a number of trials were—

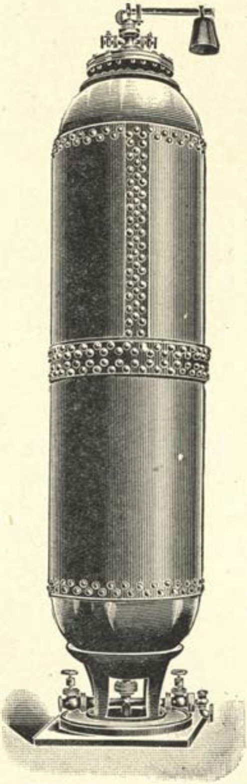

Fig. 113.—Autoclave.

Time in Hours.	Unsaponified Grease Reckoned per 100 parts Originally Employed.
4¼	9·4
5¾	5·8
7½	3·1

During the first hour or two the rate of decomposition of the fats employed was rapid, from ⅔ to ¾ being converted at the end of 2 hours; subsequently the action was much slower, becoming practically complete at the end of 6 to 6½ hours, not more than about $\frac{1}{20}$ then remaining unconverted.

The following analyses indicate the composition of the "rock" obtained by the autoclave process; they principally differ from those above cited for open pan rock, in that whereas in the open pan process excess of lime is used so that the rock contains all the fatty acids as lime soap; in the autoclave lime process a deficiency of lime is employed, so that the fatty acids are obtained partly as lime soap and partly as free acids :—

	I.	II.	III.
Lime present as lime soap (CaO), . .	3·20	2·38	2·52
Fatty anhydrides combined therewith, .	31·90	22·62	23·94
Free fatty acids, ...	57·75	58·50	66·30
Unsaponified glycerides, . . .	5·90	6·60	3·20
Unsaponifiable organic matter, . .	0·70	1·33	1·85
Grit and mineral matters; water, . .	0·55	8·57	2·19
	100·00	100·00	100·00

100 parts of the fatty glycerides used originally represent about 95 of free fatty acids and 92 of fatty anhydrides, whence 100 parts of rock represent in these three cases respectively about 95, 86, and 96 parts of fatty glycerides that have been saponified and hydrolysed; whence the proportions of glycerides not acted upon are—

$$\text{I. } \frac{5{\cdot}90}{95 + 5{\cdot}90} \times 100 = 5{\cdot}8 \text{ per cent.}$$

$$\text{II. } \frac{6{\cdot}60}{86 + 6{\cdot}60} \times 100 = 7{\cdot}1 \quad ,,$$

$$\text{III. } \frac{3{\cdot}20}{96 + 3{\cdot}2} \times 100 = 3{\cdot}2 \quad ,,$$

In general, with unadulterated tallow, the autoclave process, properly worked, saponifies and hydrolyses about 95 per cent. of the glycerides used, leaving some 5 per cent., or $\frac{1}{20}$, unacted on; if, however, too low a pressure be applied, the proportion of undecomposed glycerides may amount to considerably more than this unless a proportionately longer time be allowed, involving greater cost for fuel, labour, etc.

The "separation cake" or mixture of fatty acids obtained by decomposing with sulphuric acid the "rock" formed in the autoclave or open can process consists of the solid fatty acids produced (chiefly stearic and palmitic); the liquid acids (mainly oleic); and whatever undecomposed glycerides and unsaponifiable organic matters may be present; the latter two ingredients obviously vary with the degree of perfection or imperfection attained in saponification, and with the purity of the materials.

The ratio between solid and liquid fatty acids also varies somewhat with the character of the tallow and other fatty matters used; in general, it is not far from 2 to 1. In examining such materials, the author (*Alder Wright*) found the determination of the iodine value particularly useful, especially in the case of press cake in different stages of pressing. The further the pressing (hot after cold) is carried, the smaller the quantity of oleic acid left in the " stearine " ; but no amount of hot pressing will completely eliminate unsaturated " acids,[1] from 1 to 2 per cent. being retained even when the pressing has been carried to the utmost possible extent permissible for commercial purposes in the preparation of articles of exceptionally high melting points, and larger proportions up to 4 or even 5 per cent in products less thoroughly hot pressed. Even repeated crystallisation from alcohol of a mixture of palmitic and stearic acid does not succeed in removing all the oleic or other iodine-absorbing acid present. Thus the following typical figures may be cited, obtained with the fatty acids manufactured from a mixture of tallow and palm oil :—[2]

	Percentage of Oleic Acid calculated from Iodine Value.	Melting Point in Capillary Tube.
		°C.
Separation cake (mixture of fatty acids before pressing), ...	32·0	...
Cold-pressed cake, ...	11·5	52·8
Once hot pressed, ...	5·6	54·2
Twice ,, ...	2·5	56·1
Three times hot pressed, . . .	1·3	56·2
,, twice recrystallised from alcohol, ...	0·8	56·25
Red oils (oleine) from cold pressing, .	71·5	...
Grease from hot pressing, . . .	14·9	51·6

The percentage of solid fatty acids contained in red oils can be approximately calculated from the determination of the oleic acid, reckoning 111·02 parts of acid per 100 of iodine consumed, as indicated by the equation—

$$\underset{\text{Oleic Acid.}}{C_{18}H_{34}O_2} + I_2 = \underset{\text{Saturated Iodine Addition Product.}}{C_{18}H_{34}I_2O_2}.$$

If the percentage of unsaponified grease and unsaponifiable organic matters present be known $= a$, and that of oleic acid thus determined $= b$, the percentage of solid fatty acids is approximately $100 - (a + b)$.

Muter's process for the determination of the proportion of oleic acid present in a mixture of that substance with solid fatty acids (stearic and palmitic) is based on the solubility of lead oleate in ether. In the case of a glyceride, a quantity of substance not exceeding 1·5 grammes is saponified with excess of alcoholic potash ; with free fatty acids it is dissolved in the same solvent ; water is added and the alcohol boiled off ; dilute acetic acid is then added to neutralise excess of alkali, until a decided permanent turbidity is produced, and then

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[1] Possibly isoleic acid (m.p. 45°), and not oleic acid remains.

[2] When a pressed stearine is examined, presumably only containing a small percentage of oleic acid, 5 grammes may be conveniently taken for analysis ; on the other hand, with a substance containing a high percentage of oleic acid, proportionately less should be weighed out, usually from 0·2 to 0·4 gramme.

dilute potassium hydroxide solution with continuous agitation until the liquid *just clears again.*

The clear solution is then precipitated by lead acetate in slight excess, and stirred until the lead soap settles thoroughly; the supernatant liquor is poured off, and the precipitate washed by boiling with a large bulk of distilled water and decanting. Perfectly neutral lead stearate + palmitate + oleate is thus obtained. The precipitate is transferred to a flask of about 100 c.c. capacity and digested for some hours (with frequent agitation) with absolute ether; the ethereal solution of lead oleate is filtered into a stoppered graduated tube holding 250 c.c., and the filtrate and washings decomposed by agitation with about 20 c.c. of a mixture of 1 volume strong hydrochloric acid and 2 volumes water.

Finally, a known fraction of the ethereal fluid is drawn off and evaporated to dryness; whence the weight of oleic acid is calculated. The ethereal solution is conveniently drawn off by means of a side tap fixed to the graduated tube about one-fifth of the way up from the bottom, so as to be above the level of the acid watery fluid (" Muter's oleine tube "); or it may be blown off by means of a wash-bottle device (*cf.* p. 170).

De Schepper and *Geitel* have constructed the table quoted below, exhibiting the relative proportions of commercial " oleine " (impure oleic acid) of solidifying point 5·4°, and commercial " stearine " (stearic and palmitic acids) of solidifying point 48° present in a sample of separation cake of given solidifying point (compare pp. 93, 95).

Solidifying Point of Separation Cake.	Percentage of Commercial	
	Stearic Acid.	Oleic Acid.
Degrees C.		
5·4	0	100
10	2·5	97·5
15	6·6	93·4
20	12·1	87·9
25	18·5	81·5
30	27·2	72·8
32	31·5	68·5
34	36·6	63·4
36	43·0	57·0
37	46·9	53·1
38	50·5	49·5
39	54·5	45·5
40	58·9	41·1
41	63·3	36·7
42	68·5	31·5
43	73·5	26·5
44	78·9	21·1
45	83·5	16·5
46	89·0	11·0
47	94·1	5·9
48	100·0	0

The "filter cake" obtained from the red oils when these are chilled and passed through a filter press varies considerably in composition. In addition to particles of fibre (derived from filter press coverings, etc.) and dust, etc., filtered out, portions of unsaponified grease separate in the solid state from the cooled red oils, and smaller quantities of unsaponifiable matters (cholesterol, etc.) contained in the grease originally used.

The following analyses represent its usual composition :—

Free fatty acids, solid,	54·2	51·4
„ „ liquid (oleic acid),	25·0	21·5
Unsaponifiable glycerides,	11·2	12·3
Unsaponifiable organic matters,	4·3	4·9
Fibres, dust, etc.,	5·3	9·3
	100·0	100·0

Since the great majority of the unsaponified glycerides contained in the rock find their way into the red oils, whilst these latter constitute the smaller half of the fatty acids obtained (the "stearine" amounting to upwards of 50 per cent. of the total acids) it results that the percentage of unsaponified glycerides present in the red oils is usually more than double that in the separation cake. The same remark applies to the unsaponifiable organic matters.

If the red oils be distilled by means of superheated steam the unsaponified glycerides present are, for the most part, hydrolysed during the operation, so that "distilled oleine" is practically free from glycerides. On the other hand, a small proportion of the oleic acid becomes decomposed during the process, forming hydrocarbons (compare p. 367), so that the unsaponifiable organic matters usually become notably increased in amount. The following analyses indicate the composition of different samples of red oils and "distilled oleines," and illustrate these points :—

	Red Oils.		Distilled Oleines.	
	Tallow and Palm Oil.	Tallow only.		
Free fatty acids,	86·5	87·85	90·0	89·65
Unsaponified glycerides,	11·7	11·30	1·6	2·95
Unsaponifiable organic matters, hydrocarbons, &c.,	1·8	0·85	8·4	7·40
	100·0	100·00	100·0	100·00

Analysis of Red Oils, Separation Cake, and Similar Products.—This is carried out substantially in the way indicated on p. 177. The acid value, A, being determined, and also the saponification value, K, the data are obtained for calculating the percentage of free fatty acids and unsaponified glycerides present if the mean molecular weight of the fatty acids is known or assumed. The unsaponifiable organic matters being determined (by the methods described on p. 169) and the percentage of these constituents subtracted from 100 (as also that of any water or other foreign substance accidentally present), a sufficiently close approximation to the truth is obtained by multiplying the difference, D, by $\frac{A}{A + (K - A) \times 1{\cdot}05}$ for the percentage of free fatty acids, and by $\frac{(K - A) \times 1{\cdot}05}{A + (K - A) \times 1{\cdot}05}$ for that of the undecomposed glycerides; for if E be the mean equivalent of the fatty acids, E + 12·67 is that of the glycerides (p. 225 *et seq.*); and as E usually lies between 255 and 285, the ratio of E to E + 12·67 will lie between 1 to 1·050 and 1 to 1·045, and may safely be taken as 1 to 1·05; so that the weights of free fatty acids and glycerides will be substantially in the ratio of A to (K − A) × 1·05, whence the percentages will be—

$$\text{Free fatty acids} = \frac{A}{A + (K - A) \times 1{\cdot}05} \cdot D.$$

$$\text{Glycerides} = \frac{(K - A) \times 1{\cdot}05}{A + (K - A) \times 1{\cdot}05} \cdot D$$

Thus supposing that a given substance contains 5 per cent. of unsaponifiable matter, etc., and consequently that D = 95; if the acid value, A, be found = 175·0 and the saponification value, K, = 195·0, so that K − A = 20, the composition will be—

$$\text{Free fatty acids } \frac{175}{175 + 20 \times 1{\cdot}05} = \frac{175}{196} = 89{\cdot}28$$

$$\text{Glycerides } \frac{20 \times 1{\cdot}05}{175 + 20 \times 1{\cdot}05} = \frac{21}{196} = 10{\cdot}72$$

Unsaponifiable matter, etc., . . = 5·00

100·00

From these figures it results that the value of E is close to 286; for 1,000 parts of substance contain 892·8 of free fatty acids neutralising 175·0 of KOH; whence

$$175{\cdot}0 : 56{\cdot}1 :: 892{\cdot}8 : x = 286{\cdot}2$$

Similarly the mean equivalent of the glycerides is close to 286·2 + 12·67, or nearly 299.

Several attempts have been made to substitute metallic oxides for lime in the autoclave lime process, more especially magnesia and zinc oxide. At ordinary pressure these bodies usually act upon fatty glycerides (such as tallow) appreciably more slowly than lime, probably on account of their greater insolubility in water; but it is claimed that under pressure this difference is not observed, but rather the contrary, so that a much smaller proportion of zinc oxide will effect the saponification and hydrolysis of fatty matter than is necessary in the case of lime.

Thus in the British patent specification of *Poullain*, *E. F. Michaud*, and *E. N. Michaud* (No. 5,112, 1882) from 2 to 5 parts of zinc oxide are directly to be used per 1,000 of fatty matter (0·2 to 0·5 per cent.), heat being continued for three to four hours under a pressure of 100 to 130 lbs. (7 to 9 atmospheres). It is claimed that the smaller proportion of base employed renders it necessary to use much less acid to obtain pure free fatty acids than would otherwise be required; whilst for certain purposes—*e.g.*, manufacture of scouring soaps—it is not necessary to dissolve out the zinc at all. As regards magnesia, comparative experiments with lime and magnesia show that the action of the latter is always inferior to that of the former.[1]

A somewhat analogous process has been proposed, in which ammonia is used as saponifying agent, fatty substances and aqueous ammonia being heated together under pressure (*Barbé* and *Garelli*, Eng. Pat. 12,210, of 1907). Ammonium soaps, if formed, are so far wanting in permanency that by blowing steam through them they are decomposed, ammonia passing off (collected for use over again), whilst free fatty acids and glycerol solution remain. It does not appear that this system has as yet been adopted so largely as to rank as an established practical manufacture; but if sufficiently complete decomposition is obtainable in a moderate time, *a priori* the method would seem to be of a workable character.

In a later patent of *Barbé* and *Garelli* (Eng. Pat. 9,758, of 1908), the fat is hydrolysed by means of steam at 130° to 160° C. under a pressure of 3 to 6 atmospheres, in the presence of 0·5 per cent. of ammonia, which acts as a catalyst, after 8 hours' hydrolysis is complete and a very pure glycerol water is separated.

Stein, *Bergé*, and *de Roubaix* have patented (German Pat. 61,329) the use of solution of sulphurous acid or alkaline bisulphite as hydrolytic agent. From 2½ to 3 per cent. of solution is added to the fat in a pressure vessel, and the temperature raised to 170° to 180° C., whereby a pressure of some 18 atmospheres is attained; the reaction is said to be complete in about nine hours. The temperature should not exceed 200° C.

Hydrolysis of Fats by means of Sulphuric Acid.—It has long been known that free fatty acids can be separated from glycerides by acting upon them with sulphuric acid, the glycerol being largely converted into glycerosulphuric acid (p. 205), subsequently more or less decomposed by the heat, and the fatty acids being to some extent similarly acted upon, especially in the case of oleic acid.

The "*Wilson*" *process* (sometimes called the "Dubrunfaut" process), the outcome of various methods originally patented in England by *Gwynne*, *Jones*, and *Wilson* (*Price & Co.*), in 1840 to 1843, substantially depends on these reactions, with the further addition of purification of the fatty acids by distillation with superheated steam. The melted fats (more especially palm oil) are heated in a stout copper vessel (the "acidifier") to about 300° to 350° F. (149° to 177° C.), by

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[1] *J. Soc. Chem. Ind.*, 1893, xii., 163.

means of superheated steam. Sulphuric acid is then run in to the extent of 3 to 5 per cent., and the whole intermixed and allowed to stand some hours. During this period the glycerides are broken up, and foreign organic matters present are, for the most part, carbonised. In general, the less the quantity of sulphuric acid used, the higher is the temperature employed.

The acid mixture is then run off and boiled up with water by means of wet steam, so as to wash out sulphuric acid and other products soluble in water. Then, after standing for some hours to settle, the crude fatty acids are separated and heated to about 240° F. (116° C.) to complete the removal of water; and finally superheated steam at a higher temperature is passed through, the precise temperature varying with the nature of the fatty matter used, but being usually near 560° F. (294° C.).

Under these conditions the fatty acids are volatilised, and are condensed together with most of the steam in a series of copper serpentine refrigerating pipes exposed to the air, the escaping vapours being deodorised as far as possible by a water shower to absorb acrolein, etc., and subsequently burned, much as in the somewhat analogous case of rendering animal fats (p. 329). The fatty acids thus obtained contain a much larger proportion of solid acids, and less fluid oleic acid than those obtained by the lime saponification process from the same material, whether by the open pan or autoclave method. It would seem very probable that this is due to the transformation by the action of sulphuric acid of oleic acid into isoleic acid (melting at about 45° C.), as in the case of the action of zinc chloride on oleic acid (p. 203); or, possibly, stearolactone or oxystearic acid is formed.

According to *Lant Carpenter*[1] tallow which will only yield about 50 per cent. of its weight of candle material when treated by the lime process, gives by the sulphuric acid process at least 75 per cent. of such material of but slightly inferior quality. Of this, about three-fourths is ready for candle-making without further treatment; the other fourth, when pressed and re-distilled, yields some 75 per cent. of its weight of stearic acid, and 25 of oleic acid; ultimately, only about 5 parts of oleic acid per 100 of fat are obtained.

A considerable proportion of black pitch (often amounting to 15 per cent. and upwards) is obtained as a by-product, whilst the glycerol obtainable from the acid liquors, etc., is much less in quantity and more costly to isolate than that from the lime process. Accordingly, whilst the larger yield of solid fatty acids renders the acid method more economical from one point of view, it must be taken into consideration, *per contra*, that pitch instead of oleine is obtained as part of the product,[2] and that glycerol is lost, thus materially diminishing the apparent advantages.

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[1] Spon's *Encyclopædia*, 581, *et seq.*

[2] By distillation at a higher temperature, the pitch left on the first distillation affords a certain proportion of fatty acids of inferior quality.

Fig. 114 illustrates the general character of the plant used in the process.[1] A is the tank into which the tallow, etc., is melted by means of a steam jet directed upwards into the bung-hole of the cask. B, one of a series of lead-lined tanks, in which the grease is heated before treatment with sulphuric acid, so as to boil off water. C, pump with suitable taps and connections enabling it to pump up the hot grease into the "acidifier," D; or into the tank, H, supplying the still, I, after the sulphuric acid has been washed out with water. E, acid tank supplying acidifier. F F, superheaters. G G G G, washing vats, where the acidified grease is boiled up with water and steam to wash out sulphuric acid, etc. H, grease tank supplying still, I, through which superheated steam is blown, the vapours being condensed by the refrigerator, K, and copper cooling coils contained in the tanks, *k*.

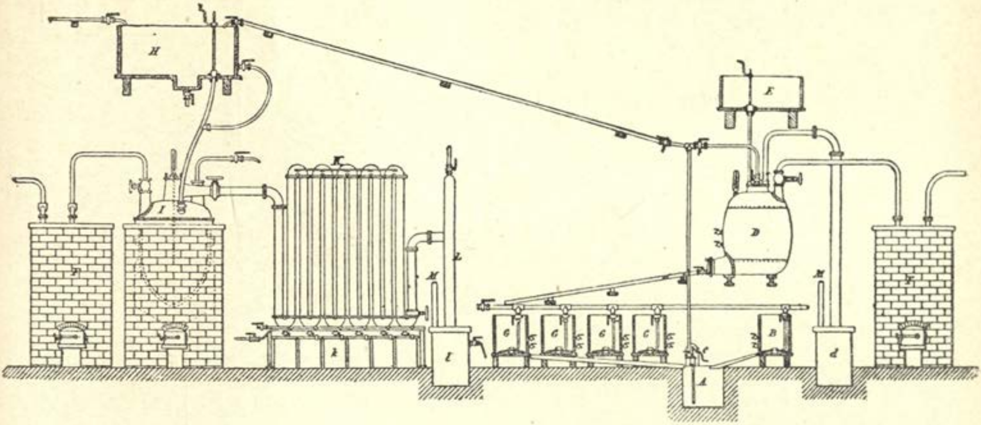

Fig. 114.—Plant for Hydrolysis of Fats by means of Sulphuric Acid.

L, scrubber to condense acrolein, etc. M, pipe leading uncondensed vapours, etc., away to combustion flue for destruction.

Fig. 115 represents Knab's apparatus for continuous distillation by superheated steam. A is the distillation vessel, into which the fatty acids to be distilled are run through the supply funnel, C, at intervals regulated by the rising and falling of the float valve, D. Superheated steam enters by the pipe, F (furnished with regulating valve and safety valve, E), and passes in small streams through the melted fatty acids from the horizontal coil at the base. The vapours pass off through the neck, G, to the condenser, the most easily condensed fatty acids being collected in H, and drawn off from time to time through the cocks, J J, whilst the other vapours pass on. K K is a blow-off pipe for removing residual pitch at intervals, the supply of fatty acids through C being temporarily shut off. Heat is applied by means of

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[1] L. Field, "Cantor Lectures," 1883 (*J. Soc. Arts*, xxxi., 861).

a bath of molten lead or other suitable metal contained in the outer pan, B.

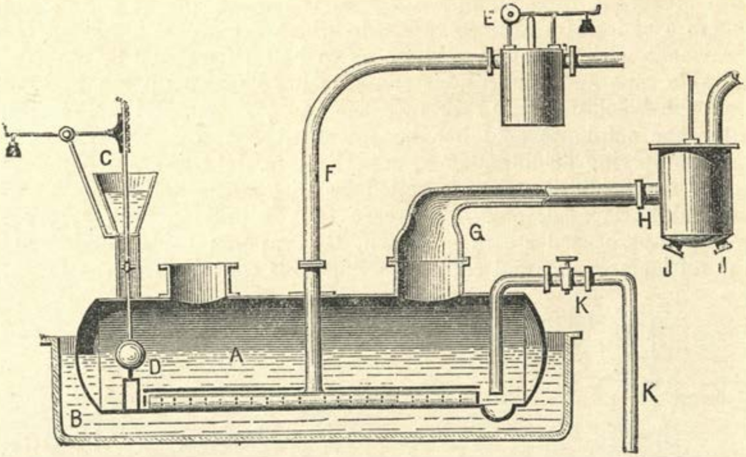

Fig. 115.—Knab's Apparatus for Distillation by Superheated Steam.

According to *Schädler*, the quantities of steam required for the distillation of a given quantity of fatty acids at different temperatures are as follows :—

Temperature.	Weight of Steam for 1 part of Fatty Acids.
° C.	
200 to 230	7 parts.
230 to 260	3 to 4 parts.
290	2 parts.
325 to 356	1 part.

When the distillation temperature does not exceed 240°, the distilled fatty acids are almost white ; at 260° a little coloration is manifest ; at 290° this is more marked, whilst at temperatures above 300° the distillate is yellow or brown.

Numerous other forms of apparatus for effecting distillation by means of superheated steam have been constructed for particular purposes—*e.g.*, the purification of grease from cotton-seed foots (p. 347), of Yorkshire grease (p. 362), and similar substances ; for the most part these differ from the above arrangements more in details of construction than in general principles.

In *Marix*' arrangement for the distillation of free fatty acids produced by hydrolysis or otherwise an air pump is applied, so that a temperature of 250° to 255° suffices for the distillation under diminished pressure. A similar process has been patented by *Lewkowitsch* (Eng. Pat. 5,985, 1888), the pressure being reduced by 10 to 13 lbs., so that a temperature of about 460° F. (238° C.) suffices, instead of about 600° F. (316° C.).

It is noticeable that when the products of distillation of a charge of given material are collected in separate fractions, it is found that in some cases the portions first passing over melt at the lowest temperatures, those coming over later possessing successively higher and higher melting points; whilst with other fatty matters the reverse is the case. Thus, with palm oil the first distillate is sufficiently solid to be used for candle-making without any further treatment, whilst the later portions are softer, and must be pressed before they can be thus employed. With bone fat, on the other hand, the successive fractions show a regular increment in consistency.

The following illustrative figures are given by *Payne* as the melting points of the fatty acids collected in seven different fractions :—

Fraction.	Bone Fat.	Palm Oil.
	° C.	° C.
1	40	54·5
2	41	52
3	41	48
4	42	46
5	45	44
6	45	41
7	47	39·5

In almost all cases, however, the average melting point of the distilled fatty acids exceeds that of the crude acids before distillation.

Bock's Process.—In Wilson's process the hydrolysis of the glycerides is mainly effected under the influence of comparatively concentrated sulphuric acid at a tolerably high temperature (150° to 180° C.), and subsequently completed partly by adding water and boiling up with wet steam, and partly by distillation with superheated steam. Bock's process differs from it in that the hydrolysis is mainly effected by comparatively dilute sulphuric acid, the action of which is facilitated by the removal of the nitrogenous films or envelopes coating the fatty globules by means of concentrated sulphuric acid acting at a much lower temperature than in Wilson's process.

Tallow, etc., is heated to 115° C. in an open vat[1] and well agitated with from 4 to 6 per cent. of sulphuric acid, whereby the albuminous envelopes are charred and broken up, but little or no hydrolysis effected. Water is then added, and the blackened but still neutral fat boiled up with the resulting dilute sulphuric acid for some hours until the decomposition of the glycerides is complete, the degree being

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[1] Lant Carpenter, *British Association Reports*, 1872, p. 72; *vide* also *Dingler's Polyt. J.*, May, 1873.

judged by the mode of crystallisation of the fatty acids on cooling a sample. When complete, the acid fluid is run off and neutralised with lime, and the resulting aqueous crude glycerin solution concentrated for sale.

The blackened fatty acids are then subjected to oxidation by means of potassium bichromate or potassium permanganate and sulphuric or hydrochloric acid, or of nitric acid, bleaching powder, etc., whereby the albuminous charred matters are largely increased in density so that they subside, leaving the fatty acids of a pale brown tint. These are then washed and crystallised, and subjected to cold and hot pressure in the usual way, whereby a brown oil and a white stearine are obtained.

The solid acids thus obtained are said to be whiter, of higher melting point, and larger in quantity than those obtained from the same material by lime saponification, probably through formation of isoleic acid, stearolactone, or hydroxystearic acid, etc. (pp. 33, 45); whilst 6 to 7 per cent. of glycerin solution at 38° T. (specific gravity 1·19, containing about 70 per cent. of actual glycerol) is obtained. The plant is simple, all the operations being carried out in one vessel; and as only open steam is used there is no danger of explosion as with autoclave processes. If desired, the brown oleic acid can be distilled by means of superheated steam; or it can be converted into solid candle material (*vide infra*). 100 parts of tallow yield 95 of crude fatty acids, reduced to 93 by oxidation and washing, of which 55 to 60 parts are available as candle stearine, melting at 58° to 60° C. (136° to 140° F.).

Twitchell's Catalytic Process.—This is based upon the fact that a certain class of sulphonated aromatic fatty acid compounds has the property of accelerating the hydrolytic decomposition of fats, so that only a small amount of sulphuric acid is required for the purpose.

These compounds, the preparation of which was claimed by *Twitchell* (Eng. Pat. 4,741, 1898), are made by treating a mixture of an aromatic hydrocarbon, such as benzene, and oleic acid, or other fatty acid, with strong sulphuric acid at a temperature below 30° C.

In the case of benzene and oleic acid, the following reaction takes place, and sulpho-benzene-stearic acid is produced—

$$C_6H_6 + C_{18}H_{34}O_2 + H_2SO_4 = C_6H_4(HSO_3)(C_{18}H_{35}O_2) + H_2O.$$

Analogous compounds are obtained by the use of naphthalene, phenol, etc., and may be separated by washing the products of the reaction with water.

In using these compounds for the hydrolysis of fat, or *fat-splitting* as it is technically termed, an apparatus of the type shown in the accompanying diagram (Fig. 116) is used.

The fat is first purified by being boiled with dilute sulphuric acid in a lead-lined wooden tank A. It is then pumped into the tank, B, which is also made of wood lined with lead, and is provided with a close-fitting cover, and after being diluted with about a third of its weight of distilled water from an upper tank, it is treated with 0·5 to 1·5 per cent. of the Twitchell reagent, the maximum quantity being used for very impure fats. Meanwhile a current of live steam is admitted into the closed vessel from the coil, so as to form an emulsion, and this heating is continued for about 24 hours, when upwards of 90 per cent. of the fatty acids present will have been liberated.

It is essential that the cover of the tank must fit tightly enough to exclude air during the hydrolysis, or the fatty acids will be discoloured, and as a further precaution a slow current of steam is passed between the layer of fatty acids and the cover of the vessel during the period of standing.

After separation of the mass into layers the glycerin water is drawn off, and the fatty acids boiled up with water for 12 to 24 hours and again allowed to separate, so as to remove the remaining glycerol. The free acid is then neutralised by introducing barium carbonate (0·05 per cent. of the stock) mixed with a little water into the tank, B, and the boiling with steam continued for about 20 minutes until the liquid is neutral to methyl-orange.

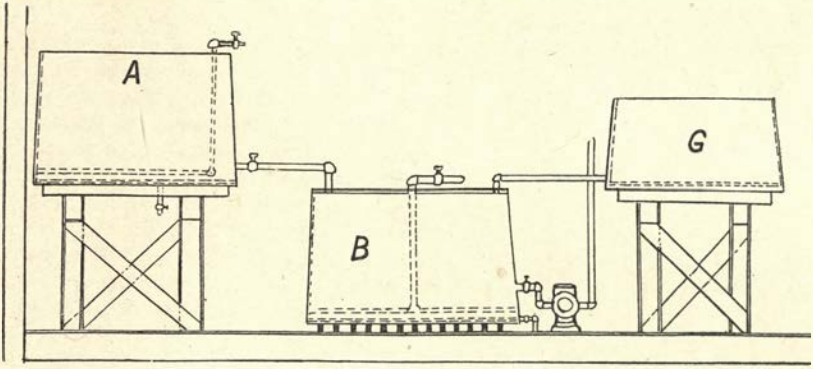

Fig. 116.—Twitchell's Catalytic Process.

A. Lead-lined covered vat.
B. Wooden vat with wooden cover, one half removable.
G. Distilled or condensed water tank.

The *sweet water* drawn off at this stage is very dilute, and is, therefore, used instead of water for the treatment of further quantities of fat.

The fatty acids (from 97 to 98 per cent. of the theoretical quantity) are crystallised and pressed, to obtain the solid acids for candle-making, whilst the glycerin is neutralised by the addition of milk of lime, and pumped into the storage tank if necessary through cloth filter.

In order to obviate the tendency to discoloration of the fatty acids in the Twitchell process, the *Vereinigte Chem. Werke Akt. Ges.*, Charlottenburg, introduced the *Dartring* saponifier (Eng. Pat. 749, 1912).

According to their process the fats are reduced electrolytically or by means of hydrogen in presence of a catalyst prior to the hydrolysis.

Sudfeldt und Co. (Fr. Pat. 463,912, 1913) attribute the discoloration to the presence of impurities in the sulpho-aromatic acids, and eliminate these by converting the mixture of sulphonated acids into alkali salts, separating the sulpho-acids by the addition of salts, and finally extracting them with a suitable solvent.

When the fatty acids obtained by Twitchell's process have a dark colour, *Happach* and *Sudfeldt und Co.* bleach them by blowing air through them. The use of this process obviates the necessity of the preliminary purification of fats prior to hydrolysis and the exclusion of air during the process (Ger. Pat. 310,387, 1913).

Lewkowitsch has shown that the sulpho-aromatic compound derived from naphthalene acts more rapidly than those obtained from anthracene or phenanthrene, but that in each case hydrolysis is practically complete after a given time—*e.g.*, 26 hours for the naphthalene compound, 39 hours for the phenanthrene compound, and 45 hours for the anthracene compound.

Reuter (U.S. Pat. 1,068,079, 1913) effects the hydrolysis of fats by heating them with successive small quantities of sulphonated fatty acids at temperatures (*e.g.*, 100° C.) insufficient to volatilise the products of decomposition, and at substantially atmospheric pressure. Air is practically excluded during the process, whilst at each stage of the treatment the aqueous glycerin and spent reagent are removed.

Petrow's "Kontakt" Process.—This process (Fr. Pat. 437,336, 1911) differs from Twitchell's original process in the fact that the hydrolysis is effected by means of sulphonated derivatives of petroleum oils or distillates. The glycerides are treated with a small amount of acid, in presence of the "Kontakt" reagent, and are agitated with steam or air during the hydrolysis.

According to a later patent taken out by the *Akt. Ges. zur Erzeug. Naphtha Sulphosauren* and *G. Petrow* (Eng. Pat. 17,148, 1914; addition to Eng. Pat. 27,244, 1911), fats are hydrolysed by means of sulphonic acids soluble in water, which are prepared by sulphonating paraffin or hydrocarbon oils derived from coal tar, lignite, peat tar, or bituminous minerals.

Happach and *Sudfeldt und Co.* (Ger. Pat. 316,455, 1911) also claim the use of sulpho-acids of petroleum distillates as hydrolytic agents. For example, sulphonated petroleum hydrocarbons are separated from the deposit of tarry matter, and washed with alkali solution, the uncombined hydrocarbons are separated from the soap solution, and the sulpho-acids are liberated by the addition of an excess of sulphuric acid. From 0·5 to 1 per cent. is required to hydrolyse fats, and the resulting fatty acids are stated to be of better colour than in the case of Twitchell's process.

Ubbelohde and *Roederer*[1] have made a series of comparative experiments, in which fats were hydrolysed under the same conditions by

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[1] *Chem. Zentralbl.*, 1917, xc., [2], 365.

means of five different hydrolytic agents (viz., naphthalene sulpho-compounds of oleic acid, of castor oil and its fatty acids, and of hydrogenated castor oil and its fatty acids), and have found that there is no difference in the speed or degree of hydrolysis.

On the other hand, the colour of the fatty acids and the glycerin water is much lighter when hydrogenated castor oil compounds are used than with the other reagents. The view formerly held that the velocity of the reaction varies with the hydrolytic agent employed must, therefore, be attributed to the fact that the preparations have contained different proportions of free sulphuric acid. The use of larger amounts of hydrolytic agent causes the emulsion to be more persistent, and thus results in more pronounced hydrolysis.

Enzymic Hydrolysis.—The lipolytic enzymes contained in certain seeds, such as castor seeds, rice, etc., effect the decomposition of oils and fats in a manner analogous to Twitchell's catalytic reagents, and technical processes are based upon this property.

The conditions underlying the hydrolysis were first systematically studied by *Connstein*, *Hoyer*, and *Wurtenberg*.[1] They showed that it was essential that there should be complete emulsification of the fat with water, and that a certain proportion of acid must be present. Typical results obtained by them are shown in the following table :—

Oil or Fat.	Grms.	Castor Seed.		Fatty Acids Liberated.	Time.	Temperature.	Acid.
		Crude.	Extracted.				
				Per cent.	Hours.	°C.	Grms. N/10 H_2SO_4.
Tallow, .	6·5	5	..	72	19	35	4
Cotton-seed oil,	6·5	5	..	84	19	35	4
Palm oil,	6·5	5	..	87	19	35	4
Arachis oil,	25	..	1·3	100	96	Ordinary	5
Linseed oil,	50	..	5	83	24	,,	10
Olive oil,	50	..	5	86	24	,,	10
Sesamé oil,	50	..	5	85	24	,,	10
Cacao butter,	50	..	5	90	24	,,	10
Cotton-seed oil,	75	..	1·5	82	44	,,	15
,,	100	..	5·0	87	44	,,	10
,,	75	..	7·5	79	24	,,	15
Triolein, .	10	..	..	50·6	24	..	..
Triacetin,	10	..	0·5	0·4	24	..	2
Tributyrin,	10	..	..	9·5	24	..	..

From these results it is evident that glycerides of lower fatty acids are hydrolysed with more difficulty than those of higher fatty acids. The amount of water promotes the hydrolysis up to a certain point,

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[1] *Ber.*, 1902, 3989.

increasing the yield of glycerol, but above that point the advantage of increased yield is balanced by the greater dilution of the product.

The degree of hydrolysis is approximately proportional to the amount of enzyme added. For example, in one of the series of experiments made by *Connstein*, *Hoyer*, and *Wartenberg* 5 grms. of castor oil hydrolysed with 0·5 grm. of extracted castor seed and 5 grms. of 2 per cent. acetic acid yielded 89 per cent. of fatty acids after 24 hours, whereas 20 grms. of castor oil with 0·5 grm. of seed and 20 grms. of 2 per cent. acetic acid yielded only 71 per cent. of fatty acids after 24 hours, and 80 per cent. after 48 hours.

Steapsin, the lipolytic enzyme of the pancreas, has a similar hydrolytic action upon oils and fats, as was shown by *Lewkowitsch* and *Macleod*,[1] but the lipase contained in the liver is more specific in its action. Thus it will hydrolyse ethyl butyrate under suitable conditions, but has little effect upon ordinary oils and fats.

The influence of water on the degree of hydrolysis was shown by *Connstein*, *Hoyer*, and *Wartenberg* by the following series of results :—[2]

Oil.	Grms.	Crude Castor Seed.	Free Fatty Acids.	Hours.	Acid.
			Per cent.		2 Per cent. Acetic Acid.
Castor oil, .	6·5	5	68	3	2 grms.
			74	18	
			74	42	
„ .	6·5	5	74	3	4 „
			80	18	
			84	42	
.	6·5	5	75	3	6 „
			84	18	
			86	42	
.	6·5	5	76	3	8 „
			87	18	
			85	42	
.	6·5	5	76	3	10 „
			86	18	
			86	42	

Welter[3] has shown that the action of the lipase of castor seed may be reversible, and that it is capable of effecting the synthesis of fatty acids and anhydrous glycerol. The equilibrium depends upon the proportion of water, a point which, as mentioned above, is of technical importance.

So far, the enzymic process of hydrolysis has not been as extensively used as *Twitchell's* catalytic process, but experiments made at the Bangalore Institute[4] have shown that it yields a pure glycerol, and

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[1] *Proc. Roy. Soc.*, 1903, lxxii., 31.

[2] Kastle and Loevenhart, *J. Amer. Chem. Soc.*, 1900, xxiv., 49.

[3] *Zeit. angew. Chem.*, 1911, xxiv., 385.

[4] *J. Soc. Chem. Ind.*, 1919, xxxviii., 5 R.

Sudborough, *Watson*, and *Varma*[1] consider that there is no reason why it should not be able to compete with *Twitchell's* method.

In practice an "extract" or aqueous emulsion of castor-oil seeds is frequently used. This contains from 55 to 60 per cent. of water, about 37 to 42 per cent. of oil, and 3 or 4 per cent. of proteins. Or the seeds themselves are ground up with about 50 per cent. of water, so as to form an emulsion, which is then separated from the husks and acidified with 0·06 per cent. of acetic acid of the weight of fat to be hydrolysed. From 50 to 80 lbs. of the seeds are required to decompose 1,000 lbs. of fat, the temperature being maintained at a temperature ranging from 25° C. for oils to about 2° C. above the melting point of fats. In no case, however, must the temperature be allowed to exceed 42° C.

The process is carried out in a lead-lined conical vessel provided with a steam coil, a pipe for injecting air, and draw-off taps at different levels. The fat is first heated with about 35° C. to the necessary temperature, being meanwhile agitated by the current of air, and is then treated with the castor seed preparation, to which about 0·2 per cent. of manganese sulphate is frequently added to accelerate the process, and with 0·06 per cent. of acetic acid calculated upon the fat. After thorough admixture for about 15 minutes the vessel is closed, and agitated from time to time for 24 to 36 hours, when about 90 per cent. of the fat will have been hydrolysed.

The process is then completed by raising the temperature to about 80° C., adding 0·2 to 0·3 per cent. of dilute sulphuric acid (2 : 1) calculated upon the weight of the fat, and continuing the agitation until the fatty acids form a melted layer on the surface. After standing for about 12 hours the liquid at the bottom, which consists of a fairly strong solution of glycerin, is drawn off, whilst the middle portion, which consists of an emulsion containing about 4 per cent. of fatty acids, is also drawn off and used for the manufacture of soap. Finally, the top layer of fatty acids is boiled with water to remove the sulphuric acid, and leaves a product particularly suitable for the manufacture of candles. The use of the extract of castor seeds instead of the seeds themselves causes the fatty acids to be of a good colour, and of better quality than those resulting from the lime-saponification process.

The *sweet water* is evaporated to about 10° Bé., freed from sulphuric acid by treatment with barium carbonate, and filtered, and the filtrate concentrated to 28° Bé. *in vacuo*. The resulting glycerin is of a light-brown colour, and yields only about 0·3 per cent. of ash.

Hydrolysis of Glycerides by Water Only.—In 1854 a patent was taken out by *Tilghmann* for the decomposition of glycerides by means of water under great pressure, and correspondingly high temperature. In one form of apparatus a mixture of fat and water was forced through a coil heated to about 420° C. (upwards of 800° F.), the pressure approximating to a ton per square inch (some 140 atmospheres). Various improvements were subsequently made; but the practical difficulties

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[1] *Ibid.*, 99 R.

attending the working of manufacturing operations of the kind prevented the method being largely adopted.

A modification of the process, patented shortly afterwards by *Wilson & Payne* (No. 1,624, 1854), effects the same result in a much simpler way. The fatty substance being heated in a still to about 300° C., superheated steam is blown through it by means of a rose jet or false bottom perforated with a large number of small holes, so that numerous jets of steam rise through the mass. Hydrolysis takes place, and the fatty acids and glycerol formed are volatilised and carried over with the excess of steam to the condensers, where the free fatty acids and glycerol in aqueous solution are obtained. The former condense first, so that by using a series of condensing chambers, little but fatty acids are obtained in the earlier ones, whilst chiefly aqueous glycerol condenses in the later ones, yielding a very pure commercial glycerin by simple concentration after separating the small quantity of accompanying fatty acids. Fig. 117 represents the general character of this plant. Steam is superheated in the superheater, A, and passes into the retort, C, covered with a lid, E; the vapours pass off to the condensers, G, for fatty acids, and F for glycerol water. If the temperature is too high (above 315° C.), much loss of glycerol occurs through the formation of acrolein.

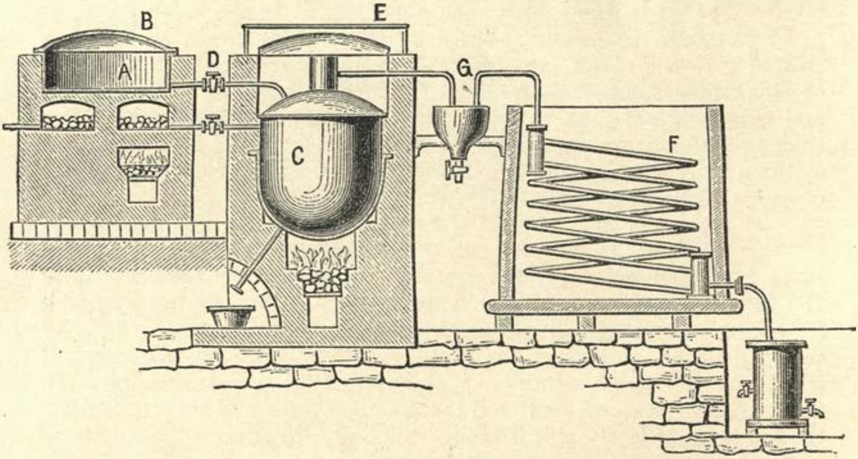

Fig. 117.—Plant for Hydrolysis of Glycerides by Superheated Steam.

In France, the saponification of fatty matters by means of water alone (without lime, etc.) is much more extensively carried out than in Britain, on account of the more frequent use of pure "stearine" candles, instead of those made largely or wholly of paraffin wax. Several different forms of apparatus are in use: for a description of some of these exhibited at the Paris Exhibition, *vide* B. Lach, *Chem.*

Zeit., xiii., 1157, 1218, 1335, 1374; in abstract *J. Soc. Chem. Ind.*, 1890, ix., 82.

Utilisation of Red Oils.—In the manufacture of candle material from glycerides a more or less considerable proportion of "red oils" is obtained, the amount varying with the method of saponification or hydrolysis adopted, the nature of the fatty matters used, and the temperature at which the cold pressing is effected.

Commercially, the "oleine" thus produced is considerably less valuable than the solid "stearine"; whence, *cæteris paribus*, it is desirable so to conduct the operations as to obtain the maximum yield of solid products and the minimum of liquid ones. In general, the red oils thus produced are utilised by conversion into so-called "oil soap," by direct saturation with soda lye of appropriate strength (*vide* Chap. XXI.); but various attempts to employ them as a source of other more valuable products have been made.

Zinc Chloride Reaction.—One such process, due to *v. Schmidt*, consists in heating the red oils with about 10 per cent. of zinc chloride to a temperature of about 185° C., whereby conversion into more solid substances is brought about, chiefly by formation of iso-oleic acid and stearolactone (*vide* p. 203).

Lewkowitsch[1] states that this process was tried on a large scale in an Austrian candle works; but proved commercially unsuccessful, owing to the yield of liquid unsaponifiable matters being too great. It is essential that the temperature of the reaction be exactly 185° C.; otherwise the proportion of liquid products is increased. It is necessary to redistil the material, and this results in a partial conversion of β-hydroxystearic acid (m.p. 82° C.) into oleic and iso-oleic acid, which greatly lowers the value of the substance.

Wilde and Reychler's Process.—*De Wilde* and *Reychler*[2] found that by heating oleic acid with a small quantity of iodine or bromine under pressure some 70 per cent. was converted into stearic acid.

This process was tried on a large scale in Belgium (*Lewkowitsch*, *loc. cit.*), but, owing to the facts that only a third of the iodine could be recovered, and the corrosive effect of the iodine vapours on the plant, it was abandoned. The substitution of bromine or chlorine for the iodine led to no better results.

Zürer's Process.—*Zurer* attempted (German Pat. 62,407) to convert oleic into stearic acid by first subjecting it to the action of chlorine, and then treating the dichloride of oleic acid formed with nascent hydrogen evolved from zinc dust (or finely divided iron or magnesium) and water heated under pressure.

The process of hydrogenation (p. 445) has now solved the problem of converting "oleine" into "stearine." A technical product thus made in Germany, prior to the war, was known as *candelite*.

Radisson's Artificial Palmitic Acid.—It has long been known that acids of the oleic family when fused with potassium hydroxide undergo a peculiar decomposition evolving hydrogen, and breaking up so as

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[1] *J. Soc. Chem. Ind.*, 1897, xvi., 390.

[2] *Bull. Soc. Chim.*, 1889, 295.

to form two acids of the stearic family, of which acetic acid is generally, if not invariably, one (p. 27); *e.g.*, oleic acid when thus treated breaks up, forming *palmitic acid* in accordance with the equation—

$$\begin{array}{ccccccccc} \text{Oleic Acid.} & & \text{Potassium Hydroxide.} & & \text{Potassium Palmitate.} & & \text{Potassium Acetate.} & & \\ C_{18}H_{34}O_2 & + & 2KOH & = & C_{16}H_{31}KO_2 & + & C_2H_3KO_2 & + & H_2. \end{array}$$

M. St. Cyr Radisson succeeded in carrying out this reaction on a manufacturing scale, converting some 3 tons of oleic acid into palmitic acid per day. The fusion was effected in a covered iron cylindrical pan or "*cartouche*" with dished base, provided with a mechanical agitator, and set in brickwork some distance (nearly 6 feet) above the fire-bars of a grate, so that a large hot air chamber was formed underneath, enabling the temperature to be more easily regulated. 1,650 lbs. of oleic acid and 2,750 lbs. of potassium hydroxide lye (specific gravity 1·4) were introduced; and when steam ceased to be evolved, a manhole in the cover was closed, and the evolved hydrogen conducted off by a pipe to a purifier and gas-holder for other use.

The temperature required to be very nicely adjusted, 300° to 310° C. being the proper value, whilst at 320° C. destructive distillation commenced. To avoid over-heating, a Giffard steam injector was provided whereby the temperature of the interior could be reduced when necessary. Some 36 to 40 hours were required for completely working off a charge, including filling the pan and emptying; the progress of the operation being judged by sampling and testing the solidifying point of the acids liberated from the mass by a mineral acid, preferably by Dalican's method.

When the reaction was complete, the contents of the pan were run off through an outlet pipe into a tank containing a small quantity of water, and the whole heated up by a steam jet. The excess of potassium hydroxide present then dissolved, forming a strong lye (specific gravity about 1·14) in which the potassium palmitate was insoluble, floating up as a soap. This was transferred to a decomposition vessel where the palmitic acid was set free by means of sulphuric acid. The acid was then distilled in the usual apparatus, leaving some 3 per cent. of pitch, and furnishing a perfectly white acid, melting at 50° to 53° C., and burning with a clear smokeless flame. About 87 per cent. of white palmitic acid was thus obtained in practice, the theoretical yield being 91 per cent. of the oleic acid used.

According to *Lant Carpenter*, the oleic acid produced by Bock's process (*supra*) was better adapted to the purpose than ordinary red oils prepared by alkaline saponification, a higher yield of palmitic acid being obtained.

According to *Lewkowitsch* (*loc. cit.*) Radisson's process had been abandoned as long ago as 1889, partly on account of the expense and of the danger of working it, owing to the evolution of so much hydrogen; and partly on account of the disagreeable odour and greasy feeling to the touch of the candles.

Redistillation of the solid acid proved to be too expensive.

Action of Sulphuric Acid upon Oleic Acid.—It has already been shown (Chap. VII.) that sulphuric acid acts upon oleic acid forming solid products of considerably higher melting point, the exact chemical reactions that occur being still the subject of discussion.

Numerous attempts have been made to utilise this reaction as a manufacturing process, but, as yet, these have not proved entirely successful from a commercial point of view.

In *David's Process*[1] the oleic acid is treated with a molecular equivalent of sulphuric acid. On the addition of water two layers are formed, the upper of which is an oily liquid consisting of 50 per cent. of a sulpho-acid not decomposed by water, and 50 per cent. of one or more of the isomerides of hydroxystearic acid. David's experiments led him to the conclusion that the [OH] group was transposable according to the temperature, so that the α-acid could be transformed into the γ-acid, or rather its anhydride.

In the industrial process the mixture of oleic and sulphuric acids is treated with water and left for an hour. The lower layer is then withdrawn and the same volume of fresh water added. The clear aqueous solution obtained yields, when exposed to a temperature of — 4° to — 5° C., about 18 to 20 per cent. of the weight of oleic acid of stearolactone (the inner anhydride of γ-hydroxystearic acid). After removal of the stearolactone and concentrating the liquid, a crop of crystals of hydroxystearic acid is deposited after twelve hours. If, on the other hand, the liquid is kept over-night at a temperature of — 4° to — 5° C., a fresh crop of crystals of stearolactone is obtained; and the filtrate from these, on being exposed to the cold for twenty-four hours, yields still more; and so on, so long as any hydroxystearic acid remains in the liquid.

In this way *David* obtained, on a manufacturing scale, 50 per cent. of solid products from a given weight of oleic acid with sulphuric acid of 65° B.: and he concluded that by the use of more concentrated acid (66° B.) the yield would be increased to 70 or even 80 per cent.

Lewkowitsch,[2] on repeating David's experiments, could only obtain β-hydroxystearic acid with traces of stearolactone.

Lewkowitsch (*loc. cit.*) made a series of valuable experiments on the same lines, both on a laboratory and manufacturing scale.

Chilled sulphuric acid was introduced drop by drop into oleic acid cooled to 0° C. on ice, so as to keep the temperature below 5° C., though in the manufacturing experiments it rose to 25° C. without apparent detriment.

The semi-solid product obtained was boiled with water, and repeatedly washed to eliminate the sulphuric acid. The time of standing did not appear to be an important factor in the results, though the strength of the acid had an influence. Thus acid containing 100 per cent. or more of H_2SO_4 yielded a product that was liquid at the ordinary temperature, and gave an emulsion with water. A similar result

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[1] *Comptes Rendus*, 1897, cxxiv., 466.

[2] *J. Soc. Chem. Ind.*, 1897, xvi., 390.

was observed when ordinary oil of vitriol was used at a temperature of 132° C.

The best results were obtained with acid of about 95 per cent. strength working at a low temperature. At 130° C. the loss was considerable.

The crude product obtained by the action of 1 molecule of 95 per cent. sulphuric acid on 1 molecule of oleic acid had the following chemical characteristics:—Acid value, 157·8; saponification value, 179·2; and iodine value, 31·8. In a parallel experiment on a manufacturing scale the corresponding constants were:—Acid value, 98·4; saponification value, 198·3; and iodine value, 24·8.

The following table shows the percentage yielded on distilling the crude products with superheated steam:—

	Crude Product.	Laboratory Experiment.					
No.	1 Mol. of Oleic Acid and 1 Mol. of H_2SO_4.	1st Fraction.	2nd Fraction.	3rd Fraction.	4th Fraction.	Residue.	Loss.
1	H_2SO_4 = 95 per cent., .	27·4	42·7	20·4	1·9	4·0	3·6
2	,, = 100·5 ,, .	26·6	46·5	17·6	...	6·2	3·1
3	,, = 103 (fuming), .	19·5	16·9	33·7	14·9	11·7	3·3

	Crude Product.	Works Experiment.					
No.	1 Mol. of Oleic Acid and 1 Mol. of H_2SO_4.	1st Fraction.	2nd Fraction.	3rd Fraction.	4th Fraction.	Residue.	Loss.
1	H_2SO_4 = 95 per cent., .	30·0	30·0	26·5	...	6·2	7·3 (exceptional)

The yields obtained on treating 1 molecule of oleic acid with 2 molecules of sulphuric acid were considerably less.

The constants of the different fractions obtained in the first experiments were as follows:—

	Laboratory Experiment.				Works Experiment.			
	1st Fraction.	2nd Fraction.	3rd Fraction.	4th Fraction.	1st Fraction.	2nd Fraction.	3rd Fraction.	4th Fraction.
Iodine value, .	58	84·3	83·8	82·4	82·8	85·2	65·8	77·4
Acid ,, .	192	196·5	196·9	188·1	197·5	197·3	149·1	197·5
Saponification value, . .	201	201·2	199·9	194·9	200·7	200·7	188·9	201·3
Melting point, °C, . .	Liquid	27·2-28·3	27·2-29	25·5-29	20·2	25·3	24·9	23·45

Since the melting points of the best fractions are still low, the distillation method appears unlikely to yield commercially profitable results, but *Lewkowitsch* considers that a separation of the β-hydroxystearic acid (m.p. 82° C.) by hydraulic pressure, so as to avoid its decomposition into oleic and iso-oleic acid during the distillation, is more promising.

In a process patented by *Magnier*, *Brangier*, and *Tissier* (Eng. Pat. 3,363, 1900) the fatty material is treated with sulphuric acid (about 6 per cent.) at 80° C., and the resulting product mixed with water and heated in an autoclave under pressure, after which an electric current is passed through so as to decompose the water. At the end of the process the fatty acids float on the surface of the liquid, whilst the sulphuric acid and glycerol remain in the lower liquid.

CHAPTER XVIII.

MANUFACTURE OF CANDLES, TAPERS, AND NIGHTLIGHTS.

Several different kinds of process are or have been employed in the manufacture of candles for the purpose of surrounding the wick with a more or less uniform coating of solid combustible matter.

In the early and middle ages, when wax was the material used by the more wealthy classes as illuminant, a simple mechanical process of hand manufacture was usually adopted, a lump of wax being softened by heat and kneaded until sufficiently plastic, then applied round the wick, and rolled into shape.

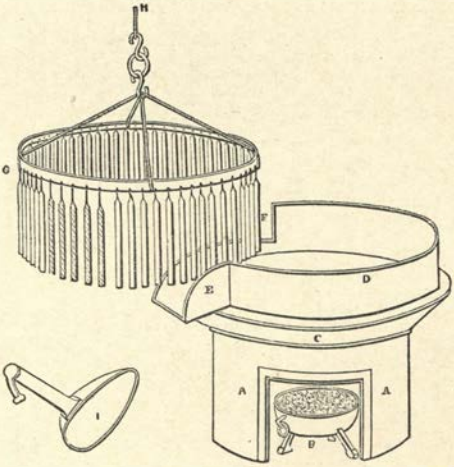

Fig. 118.—Basting Wheel.

A similar process is still employed, with the difference that the wax is applied by "pouring" the just melted material over the wick so as to incrust it with a layer of wax; after cooling, another layer is similarly poured over, and so on, the candle being reversed in position from time to time until the requisite thickness is attained.

The still somewhat plastic wax candles are then rolled into shape, some half dozen at a time, on a smooth marble table with a board on which the workman presses heavily; the finished candle consequently exhibits concentric layers of wax, something like the rings of a tree. The process requires considerable skill to produce a perfectly even surface with truly central wick, especially in the case of large sized candles. To facilitate the "pouring" or "basting" operation, the wicks are usually hung on a horizontal wheel (Fig. 118) fixed over the projecting lip of a large basin holding the melted wax, so that each is "basted" in turn. Large conical altar candles (*cierges*) are still generally made substantially by the older process, the plastic wax being rolled into a long thin strip or ribbon, which is then coiled round the wick (previously soaked in melted wax) and rolled into shape on the marble slab, instead of being basted on.

In practice it is difficult to "mould" wax candles satisfactorily on account of their sticking to the mould and shrinking during solidification, and consequently tending to crack; but thin candles can be "drawn" somewhat after the fashion of wire by running the wick through a pan of melted wax, and subsequently making it pass through a draw-plate so as to reduce the layer of wax to uniform thickness (Fig. 119).

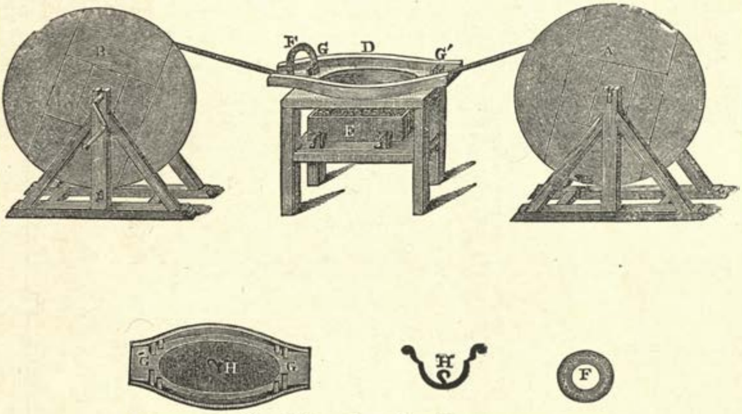

Fig. 119.—Drawing Tapers.

The wick is usually wound from one drum on to another; after one coating is applied it is wound back again, this time passing through a somewhat wider draw-hole, so as to give an increased thickness of wax. As a rule, however, neat tapers of more than about half an inch in diameter cannot be conveniently made in this way, as the tendency to crack becomes too great when the diameter increases beyond this point.

In whatever way the wick is coated, whether by "rolling," "pouring," or "drawing," the candles are ultimately finished by cutting off the butt ends with a sharp knife (Fig. 120), and trimming the other ends to conical tips. As a rule, when tinted wax candles are required, only the last batches basted on are coloured, as the tinting materials are generally apt to clog the wick, especially if solid; for white candles air-bleached wax is employed, wax blanched by chemicals (especially chlorine) being unsuitable (p. 354).

Dip Candles.—In the preparation of rough candles for household use in mediæval times and even still more recently,[1] the wicks used were generally rushes (*Juncus conglomeratus*) skilfully peeled so as to leave the pith supported by one thin rib of green rind, whence the familiar term "rush-light." These were soaked (after drying) in melted tallow or kitchen grease, held up to cool, then dipped again carefully into the just melted grease, and quickly withdrawn, so that the film of adherent tallow solidified before it had time to run down; for which purpose it was imperative that the grease should not be over-heated.

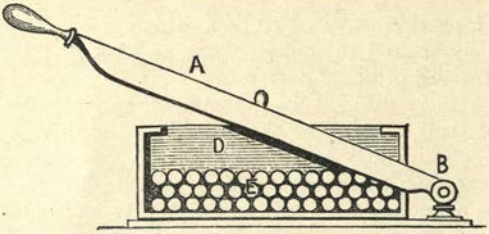

Fig. 120.—Knife for Cutting off Butt Ends of Candles.

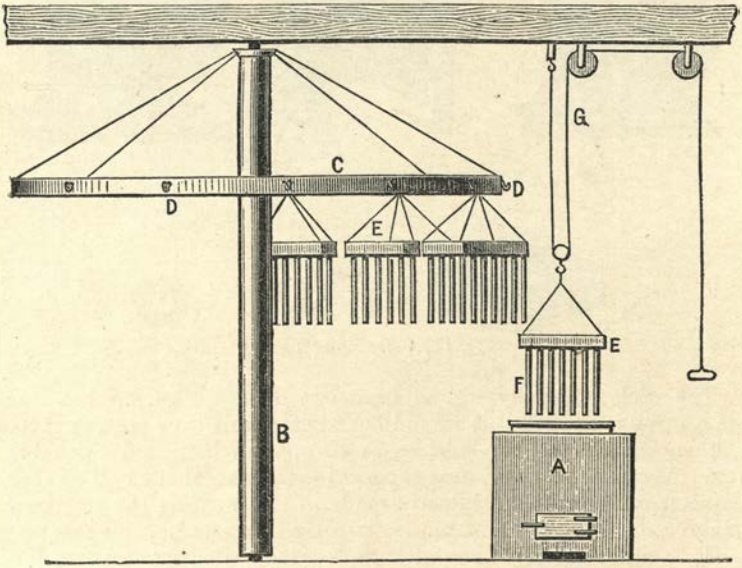

Fig. 121.—Rotating Candle Dipper.

The dipping was then repeated at intervals until the coating of tallow was sufficiently thick. By and bye when tallow candle-making

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[1] Gilbert White, *Natural History of Selborne*, 1789.

became a trade of itself, this method of manipulation was adopted on a larger scale with appropriate modifications; linen or cotton wicks supplanted rush pith, whilst the dipping was effected by fixing a number of wicks (previously soaked in tallow) on hooks driven side by side a little way apart into the bottom of a piece of board or wooden lattice-frame, so that by lifting the board by means of a knob or handle on the upper side, all the wicks attached could be simultaneously dipped and withdrawn.

To facilitate the dipping, the board with dependent candles was attached to a rope passing over a pulley (Fig. 121); each frame of candles when dipped being unhooked from the rope and suspended from the periphery of a horizontal wheel so as to hang up and harden. By dipping in regular succession each one of a number of frames thus suspended, each batch of candles became sufficiently cooled and "set" to be ready for another dip by the time its turn came. The wheel thus slowly revolved, making one revolution for each dipping of the whole series of frames. By attaching suitable weights to the end of the cord as counterpoise, the time was easily ascertained when the candles had been dipped sufficiently often to be of the right weight.

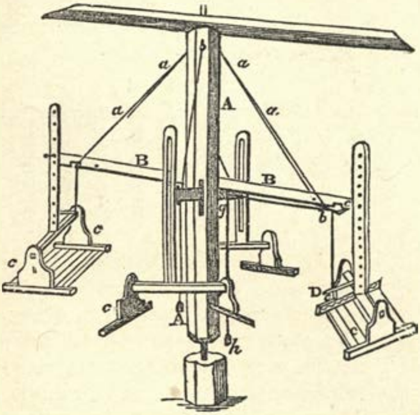

Fig. 122.—Edinburgh Wheel for Candle Dipping.

To avoid the trouble of unhooking each frame and hanging it up from the wheel, a series of separate radiating bars have been substituted for the complete wheel, each bar being capable of oscillating in a vertical plane working on a pin in a slot in the vertical axis. Fig. 122 represents a form of "Edinburgh wheel" of this description. Each bar, B B, carries two dipping frames, one at each end, the second serving as counterpoise to the first; each frame is successively pulled down and dipped in the tallow cauldron and then raised again, the wheel being made to partially revolve so as to bring the next succeeding frame over the cauldron. Various subsidiary arrangements are sometimes applied for the purpose of ensuring the horizontal position of the radiating bars when raised after dipping, even though the newly dipped end may be a little heavier than its counterpoise.

The wicks may be suspended from the hooks by means of a loop of cotton thread tied to them; but a more convenient plan is to double the wick, stringing the series over a rod as indicated in Fig. 123. The rod with the dependent wicks is then dipped by hand into a trough of melted tallow and hung up on a rack, or otherwise supported, until the tallow is sufficiently set to permit of another dipping; or a series of rods are attached side by side to a frame supported by cords and attached to an Edinburgh wheel, etc. In order to impregnate the wicks with tallow in the first instance, and to get them all of the right length, the wick is unwound from a bobbin, and wound round a square frame of suitable size so as to form a sort of loose covering. This is then dipped bodily in hot tallow to within an inch or so of the top of the frame, so as to fill up all the pores in the immersed portion of the wicking, after which the entire row of strands at the bottom of the frame is cut through with a knife, and the different doubled wicks separated, and strung on the rods as indicated.

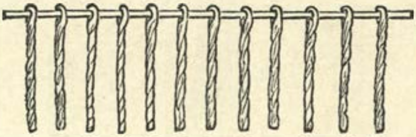

Fig. 123.—Wick Holder.

Another method, formerly much used in the larger dipping establishments, is to have the cauldron of melted tallow movable, so as to pass in succession beneath each one of a series of frames. Fig. 124 represents the section of an arrangement of the kind. The two frames, D D, are connected by a cord passing over pulleys supported by a beam and posts, so that one counterpoises the other; and thus, by pulling the cords, E E, the one or the other can be made to descend. Several of these pairs of frames are arranged side by side (fig. 125), the cauldron of tallow (kept fluid by means of a brazier) running on a railway down one side of the row and up the other, so that each one of the frames is dipped in regular rotation. A sort of mechanical wiper is conveniently connected with the cauldron, so that by moving a lever after the candles have emerged from the melted tallow, the drops of grease that run down to the bottoms are removed. When well-shaped candles are required, the irregularities may be smoothed down by pulling each candle in succession by hand through a series of holes in a draw-plate (graded in diameter, the smallest being the size ultimately required) so as to strip off a portion of the outer coating, leaving the remainder fairly cylindrical.

A peculiar modification of the dipping process is sometimes practised. The wicks are dipped in hot melted tallow as usual to fill up pores; but instead of applying the outer coatings by successive dippings of the treated wicks, thin steel rods are dipped in the tallow, and when the candles are of the desired thickness they are cooled completely, and the steel cores extracted. The wicks are then passed through instead, and fastened in position by a few drops of melted tallow. A similar device is also employed in the manufacture of certain kinds of night lights (*infra*), excepting that the wickless hollow candles are made by casting instead of dipping.

At the present day, although the manufacture of dip candles made of unsaponified tallow is by no means extinct (there being still some demand, especially in country districts), the quantity manufactured is much less than that of "moulded" candles, prepared, for the most part, from solid fatty acids (so-called "stearine") and paraffin wax, but sometimes from unsaponified tallow or mixtures containing both free fatty acids and solid unsaponified glycerides (composites).

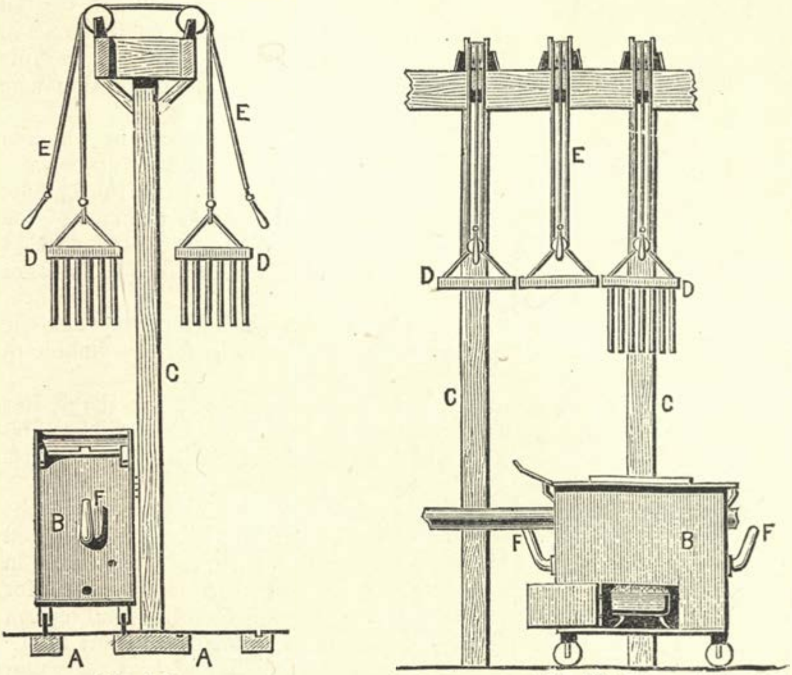

Fig. 124. Fig. 125.

Figs. 124 and 125.—Dipper with Movable Cauldron.

Tallow candles, when blown out, generally emit an acrid vapour, due to the decomposition of the glyceride by the heat of the smouldering wick, with formation of acrolein. This circumstance, together with their comparative softness inducing "guttering," the necessity for "snuffing," and the tendency to emit smoke and give a less clear brilliant light than stearine and paraffin candles, has caused them gradually to fall into comparative disuse, especially among dwellers in towns.

Wicks.—The nature of the wick employed in a candle very greatly affects the way in which it burns, and consequently the light emitted. In the old-fashioned tallow dip candle, thick twisted cotton wicks are still used. These do not thoroughly consume away, and consequently "snuffers" are required to remove the charred smouldering cotton; otherwise much less light is given out, and a smoky flame produced.

Various mechanical devices have been tried to give to such twisted wicks a tendency to bend outwards in the flame, so as to come in contact with the air and consume spontaneously; whilst attempts have been made to attain the same end by incorporating a thin wire with the cotton strands.

Palmer's "metallic wick" was an analogous device, in which a thread impregnated with powdered bismuth was bound up with a number of others of ordinary fibres by winding one round the bunch; when burnt, the bismuth formed a minute globule at the end of the wick, the weight of which tended to draw the wick outwards; so that the carbonised cotton was burnt away, and the bismuth volatilised, or was otherwise dissipated by combustion.

De Milly attempted to obtain the same result by impregnating the wicks with boric and phosphoric acids, etc., so as to form a globule of fused mineral matter.

All such devices, however, have been superseded for the better classes of candle by the use of flat plaited or "braided" wicks (first introduced by *Cambacères*), in which the mode of construction imparts a natural tendency to bend outwards.

The precise mode of plaiting adopted considerably modifies the way in which the wick burns, one kind of braiding being better suited than another for certain kinds of combustible matter. Thus, paraffin candles require a wick more tightly braided than is necessary for stearine candles, whilst looser wicks are used for wax and sperm candles. As a rule, the plaiting of the wicks is not carried out in the candle factory, but by spinners making a speciality of this particular line, and delivering the braids in hanks of convenient size; the machines used closely resemble those employed in the manufacture of ordinary braids.

Wick Pickling.—Before being introduced into candles, the wicks are soaked or "pickled" in a suitable saline solution for some hours. They are then drained and wrung out by means of a rapidly rotating centrifugal machine so as to expel almost the whole of the fluid without twisting the threads in any way, and are finally hung up to dry in a room heated by steam pipes.

The object of the pickling is, on the one hand, to counteract the accumulation of mineral matter or "ash" in the wick as it burns, and on the other, to prevent the too rapid burning away of the wick fibres before the due quantity of melted fatty matter has passed along them and been consumed in the flame. The choice of the particular solutions employed and their strengths is usually regarded as a trade secret, each manufacturer having his own views on the subject. Solutions containing from 1 to 5 per cent. of saline matter have been recommended, such as solutions of borax (alone, or acidulated with a minute quantity of sulphuric acid), sal-ammoniac, saltpetre, phosphate of ammonium, or mixtures of such salts. Although only very minute quantities of saline matters ultimately remain in the dried wicks, yet the effect produced by them on the way in which the candle burns is often very marked.

MOULDED CANDLES.

The art of moulding candles, instead of dipping them, is due to the *Sieur de Brez* in the fifteenth century; but excepting for the employment of this method in the manufacture of spermaceti candles in the latter part of the eighteenth century, but little advance was made in this direction until the introduction of "stearine" (solid free fatty acids) as candle material instead of tallow, and the subsequent employment of paraffin wax for the same purposes a little after the middle of last century.

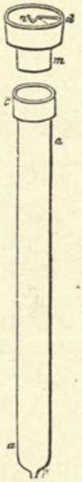

Fig. 126.—Candle Mould.

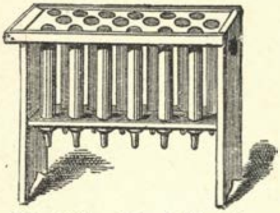

Fig. 127.—Hand Moulding Frame.

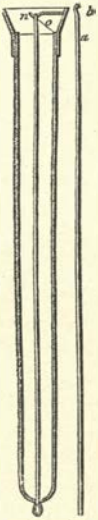

Fig. 128.—Mode of Fixing Wick.

Moulding Machines.—The earlier moulding machines were so-called "hand frames" (still in use for small operations and special sizes for which only a small demand exists) containing a series of pewter moulds with removable mouth-pieces, fig. 126, depending downwards from a shallow trough, fig. 127, the top end being lowest and the butt end uppermost. By means of a wire with a hook at the end the wick was hooked through a narrow orifice at the conical lowest end of the mould and brought upwards, and finally fixed to a wire hook, *n*, by means of a knot on the wick, or preferably a little loop of cotton thread tied to the wick; so that by gently pulling the wick downwards at the bottom and fixing it with a peg, it was stretched in the axis of the cylindrical mould (fig. 128). Or instead of a removable mouth-piece carrying a hook like *n*, a short piece of wire was passed through the loop and allowed to rest in a couple of shallow notches opposite to one another in the upper rim of the mould, so that the wick was supported axially.

Figs. 129 and 130 represent an improved modification of this arrangement, where, instead of having a separate wire for each candle, a whole row of wicks is simultaneously supported by a single rod, D D, which is withdrawn when the candles are extricated from the moulds after cooling. The use of this rod generally leaves a corresponding mark or groove at the base of the finished candle, whereby a hand-made article can be readily recognised.

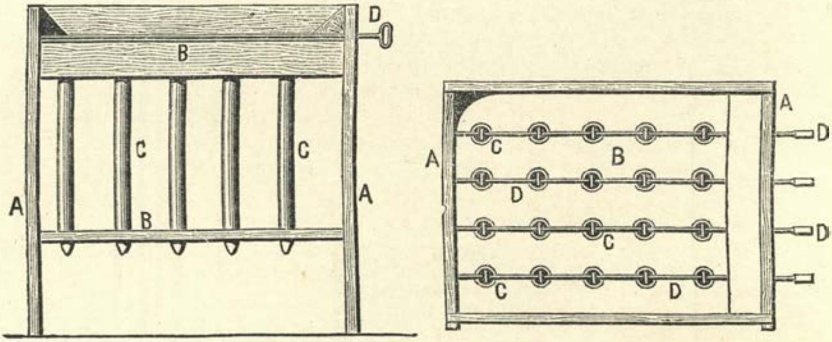

Fig. 129.

Fig. 130.

Figs. 129 and 130.—Improved Moulding Frame.

The moulds being somewhat warmed so as not to chill the candle material too quickly, the melted substance is poured into the trough so as to fill all the moulds, and also part of the trough to allow for shrinkage. The whole is then set aside to cool, and when the candles are sufficiently set, the contents of the trough are scooped out with a trowel.

Preferably, the frame carrying the series of moulds is immersed in a water tank so as to facilitate the chilling, the temperature of the water varying with the nature of the material used and the dimensions of the candles moulded. It is usually necessary, however, that the solidification should go on at a particular rate, since otherwise a crystalline structure may be developed by too slow cooling, injuring the appearance of the candle, or cracking may occur with too rapid chilling.

When the candles are completely set, the frame is removed from the water, and the candles removed by withdrawing the pegs and inverting the frame, when they usually fall out of themselves owing to the moulds being slightly conical; if sticking occur, gently tapping the mould generally suffices to dislodge the candle.

Including "threading"—*i.e.*, setting the wicks in position by hand (by passing it through the lower orifice and pulling it upwards by means of a wire)—filling, and emptying, hand frames can only be worked off about once in an hour, or somewhat less frequently. In the later "continuous" candle moulding machines, three times this speed is attained, much time being saved by a device whereby the wick is passed continuously at stated intervals through the mould, a candle being cast at each period, and when set, lifted upwards so as to draw the wick into position for the next moulding, so that a string of candles, one after the other, is cast around each wick.

Royan's Wick-Moulding Machine.—Fig. 131 represents Royan's form of continuous wick-moulding machine as used in Germany (*Schädler*). As each batch of candles is cast and becomes sufficiently hard, it is lifted upwards out of the moulds by means of a rack and pinion which elevates a platform, to the under side of which the wicks are fastened by a series of clips. In this way the wicks are always kept gently stretched along the axes of the moulds; and several successive tiers of candles are thus moulded without altering the attachments. When the platform reaches its highest elevation the

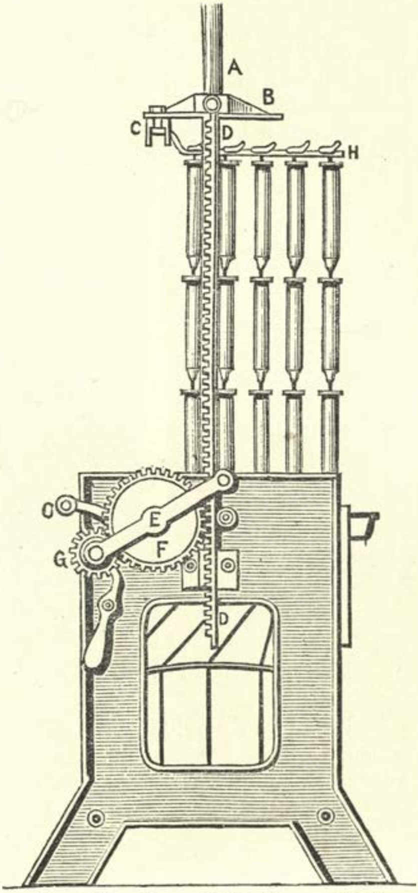

Fig. 131.—Royan's Continuous Wick Moulding Machine.

wicks are severed below the lower tier, and the strings of candles removed from the clips that support them. The platform is then lowered, the wick ends affixed to the clips, and the operations commenced afresh.

Camp's Moulding Machine.—Fig. 132 represents "Camp's moulding wheel," a combination of the principle of the "Edinburgh wheel," used for dipping candles, with this "continuous" moulding action. This arrangement has been somewhat extensively used in America (*Christiani*). A revolving horizontal wheel, B, is supported by iron rods, O O O, and turns on a pivot, C, attached to the roof. A series of moulding frames, A A A, are supported by the wheel, regularly arranged radiating from the centre. The troughs, *b b*, *b b*, surrounding these can be filled with water heated to any required temperature by means of steam pipes, or, if needed, be cooled with ice. Just below the tips of the moulds are the rows of bobbins of wick, the ends of which, to begin with, are drawn upwards by hand and adjusted in the axes of the moulds.

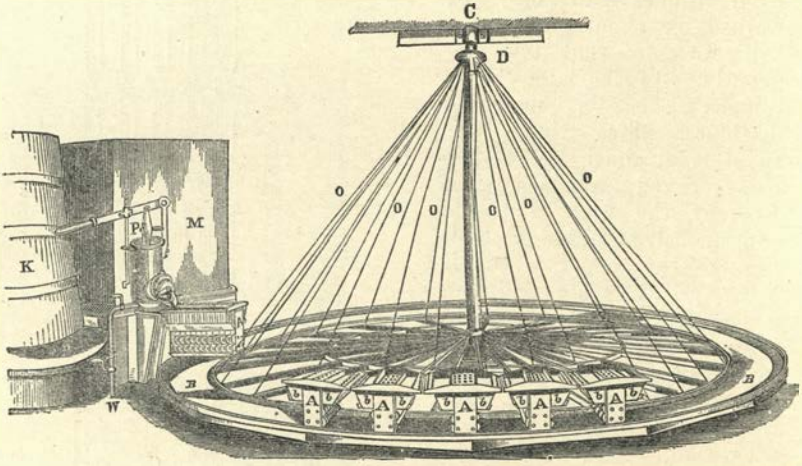

Fig. 132.—Camp's Moulding Wheel.

When all the moulds are ready the discharge valve, P, of a tank of melted candle material, M, is opened so as to fill one of the mould frames in position underneath. The wheel is then pushed round until the next mould frame is in position under the spout, when this is similarly filled; and so on with all in turn. By the time the last frame is filled the first will have cooled sufficiently to enable the candles to be cautiously withdrawn and laid over in grooves cut for their support in the ledges of the frame; and as this is done the wicks are drawn upwards, so that the moulds are threaded ready for the next filling.

The mould frame thus emptied is refilled with melted candle material; and similarly with the next, so that the wheel is revolved a second time, each mould frame being filled in succession as before. When all the frames are filled the candles lying over in the grooves (by this time perfectly hard and solid) are cut off and removed, and these now filling the moulds are pulled upwards and made to take their place.

Other Moulding Machines.—Most of the moulding machines in use at the present day in the larger factories are constructed on the "piston" principle, whereby the candles when sufficiently set are mechanically expelled from the moulds by means of a series of pistons rising up therein and lifting the candles out. Fig. 133 represents the general mode of action, identical in principle with that of an ordinary "lifting pump" without the valve, excepting that the piston-rod is below instead of above. The piston is hollowed conically so as to form the mould of the candle tip, and the wick passes upwards through the tubular piston-rod. A series of moulds is arranged in a convenient frame or trough into which water can be run heated by means of steam, or artificially cooled according to the temperature at which the moulds are to be kept, which varies with the nature of the candle material.

Fig. 134 represents a moulding machine containing two such troughs arranged side by side and attached to a closed water tank. In each of these troughs are three to eight rows (or two in the smaller machines) of moulds, numbering from 80 in the smallest to 800 in the largest machines.

Each mould is a tube open at each end. A sliding piston (tip mould) in this tube forms the point of the candle, and this is attached to a thin tube (piston-rod) made of tinned steel or wrought iron. The tip moulds, which form the nearly conical end of the moulds, are connected with a movable plate, known as the driving board, by means of the piston-rods, and are moved together by the action of a handle operating either a rack and pinion wheel or a screw.

The wicks are placed in the bottom of the machine, being wound upon bobbins corresponding with the number of moulds in the machine, from which they pass through the piston-rod and tip mould.

Fig. 133. Piston of Moulding Machine.

Above the two troughs containing the heads of the row of moulds are devices known as the "clamps," which serve to hold the candles ejected from the moulds, and at the same time keep the wicks in the centre of the moulds.

In working this machine the wicks are first drawn up and suspended, with a few inches lying loosely at the bottom of the mould. Cold water is introduced into the iron water tank, which encloses the moulds, and is heated by means of a steam jet to the required temperature. The candle material is now poured into the two troughs until the moulds are filled, and cold water is immediately turned into the water tank.

When the excess of material in the trough is solidified it is removed by means of a suitable tool.

As soon as the candles are sufficiently set (about 15 minutes in the case of paraffin candles), they are ejected from the moulds by turning the handle, the wicks being simultaneously unwound from the bobbins, and following the candles.

The candles pass through the open clamp, and when they have reached the regulated height the clamps close and retain them. The handle of the machine is then reversed until the bottom of the moulds are closed by the tip moulds, and a second filling of the material is poured into the moulds while the candles remain suspended in the clamps.

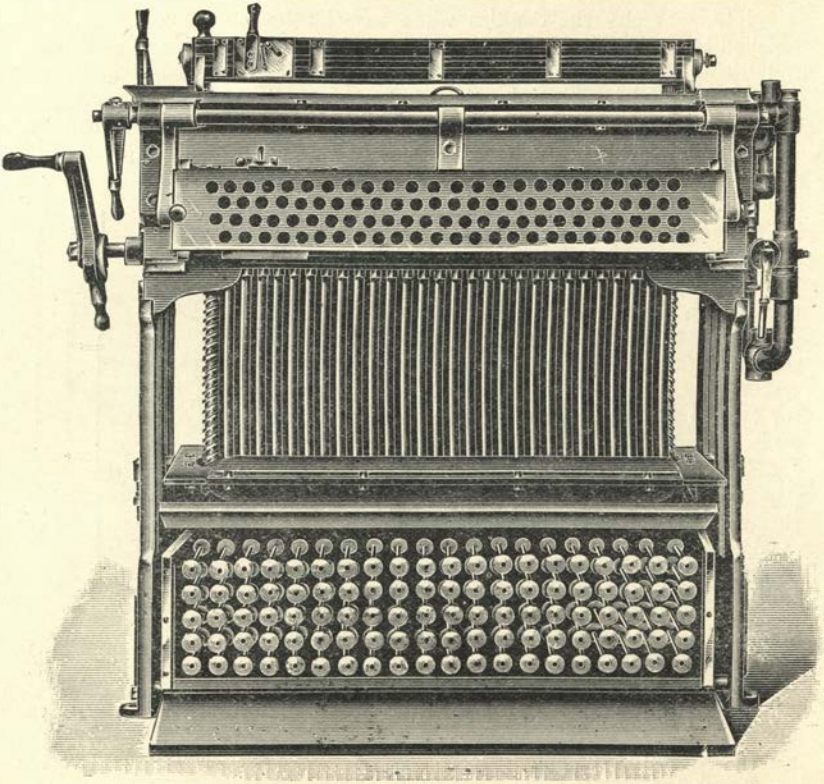

Fig. 134.—Cowles' Candle Moulding Machine (Front Elevation).

After the surplus material in the trough has solidified sufficiently, the wicks are cut by means of a special knife, the clamps containing the candles are removed, and the candles ejected into a rack.

Fig. 135 represents a special form of this machine, fitted with 300 moulds arranged in ten rows. It has been constructed so as to be readily worked by female labour, the clamps, for instance, being divided into four in order to reduce their weight.

The lengths of the candles thus moulded in a given set of cylinders can be regulated at will by simply raising the driving plate by means of set screws, so as to shorten the distance between each piston and the top of the corresponding mould, and thus form a shorter candle, or *vice versâ*. When the butt ends of the candles are required to be conical (so as to fit into any sized stick), a special kind of cutting machine is employed to shave down the ends. If the cone is to be of greater diameter at its base than the rest of the candle, a special modification of the mould is employed (*infra*).

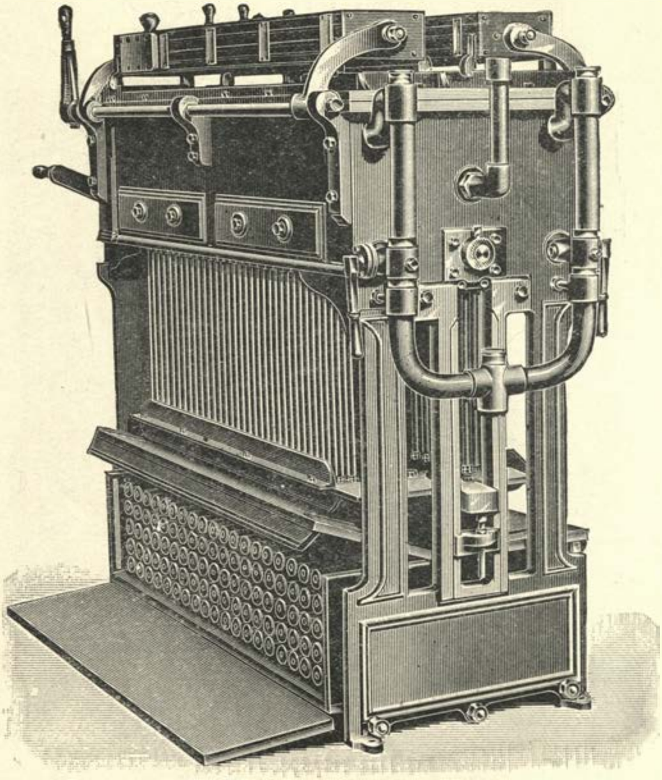
Fig. 134*a*.—Cowles' Candle Moulding Machine (End Elevation).

The chief skill required in working the candle moulding machine lies in properly regulating the temperature, the *modus operandi* varying in this respect with the material.

With pure stearine (*i.e.*, solid fatty acids with just enough paraffin wax, beeswax, or vegetable wax, or other similar material to " break the grain," and prevent or diminish crystallinity), the moulds are kept at a temperature slightly below the setting point of the candle material, which is poured in on the point of congealing, well stirred so as to form a gruel-like mass. The workman generally judges the temperature by simply putting his hand into the water trough surrounding the moulds, cooling it by running in a little cold water if necessary, or *vice versâ*.

With paraffin wax, on the other hand, the moulds must be heated

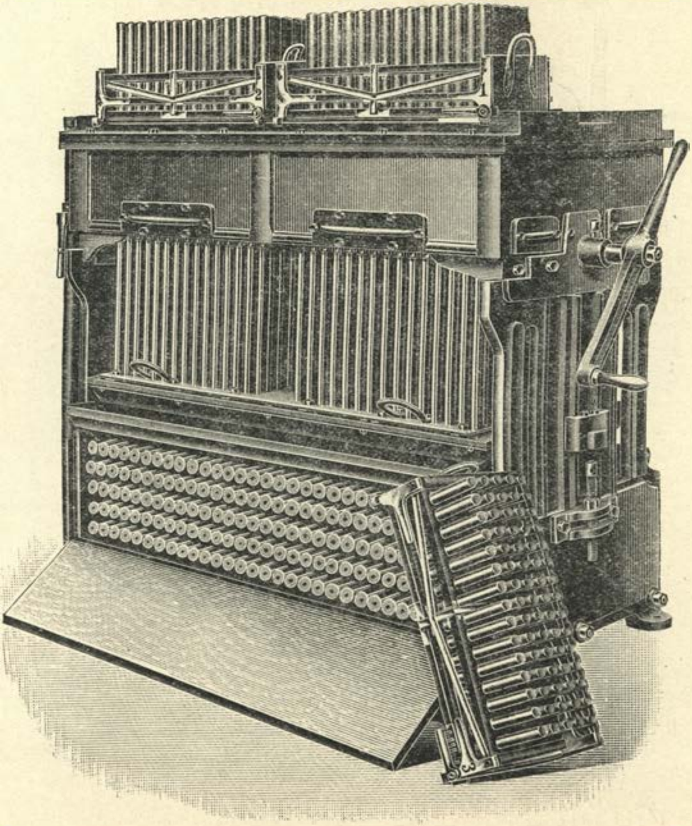

Fig. 135.—Cowles' Candle Moulding Machine, adapted for Female Labour.

by hot water or steam well above the melting point of the wax (usually up to 80° to 85°, or about 170° F.), whilst the wax also should be hotter than its melting point. When the moulds are filled, the surrounding hot water is run off and cold water run in instead, whereby the material is quickly chilled, and the peculiar translucency and lustre desired is attained.

In certain cases this effect is heightened by alternately admitting hot and cold water into the water box, the precise mode of operating varying somewhat according as paraffin scale of relatively low melting point is used, or harder paraffin (ceresin, ozokerite, etc.) of higher melting point, with or without the addition of a small percentage of stearic acid, either for the purpose of serving as vehicle for colour, or to prevent the tendency to soften and bend often shown by pure paraffin candles, even at temperatures considerably below the melting point. In some cases, where mixed materials are used with stearine in larger quantity, intermediate temperatures are employed for the water box. In Britain, paraffin candles have largely driven fatty acid candles out of the market on account of their greater cheapness, but this is not so much the case on the Continent.

Moulded *tallow* candles were formerly somewhat largely employed, but latterly, like dips, have mostly gone out of use on account of the objections to glycerides as combustible matter. The same remark also largely applies to "composites," or mixtures of free fatty acids and glycerides, except for night lights.

Spermaceti candles are usually moulded in much the same way as paraffin wax candles, the material being heated above its melting point and run into hot moulds, which are then rapidly chilled by means of cold water. During the latter part of the eighteenth century and the earlier portion of the last one they were in some considerable amount of use by the wealthier classes; but like wax candles, their use is but small nowadays as compared with candles of "stearine" and paraffin wax. With properly adjusted wicks they burn with considerable regularity and brightness, and are accordingly selected as the practical standard for photometric observations; a "standard candle" being one burning 120 grains of spermaceti per hour.

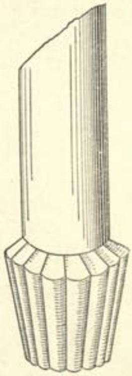

Fig. 136.
Self - Fitting
Butt End.

Candles of Special Shape.—For certain special forms of candle particular modifications of the moulding machine are required. Thus stearine candles, especially on the Continent, are often cast with longitudinal internal spaces or tubes, which tend to prevent "guttering" whilst burning. Spiral exteriors are also much in favour; formerly these were made by lathing cylindrical candles cast in the ordinary moulds; but in the more recent machines the pistons are made to ascend by a screw motion, the moulds themselves being correspondingly grooved, so that the candles are screwed out of the moulds.

For "self-fitting" butt-ends (fig. 136), where the thickest portion of the conical part is of greater diameter than the rest of the candle, the frame above described requires modification.

Machine for "Self-fitting" Candles.—Fig. 137 represents a machine for moulding self-fitting butt-end candles, constructed by *E. Cowles*, of Hounslow, in which the butts are shaped by a separate series of moulds fitting on the top of the cylindrical moulds, and ultimately lifted off from the conical candle ends by means of the chain, the candles being then raised by the piston and held in removable nipping frames in the

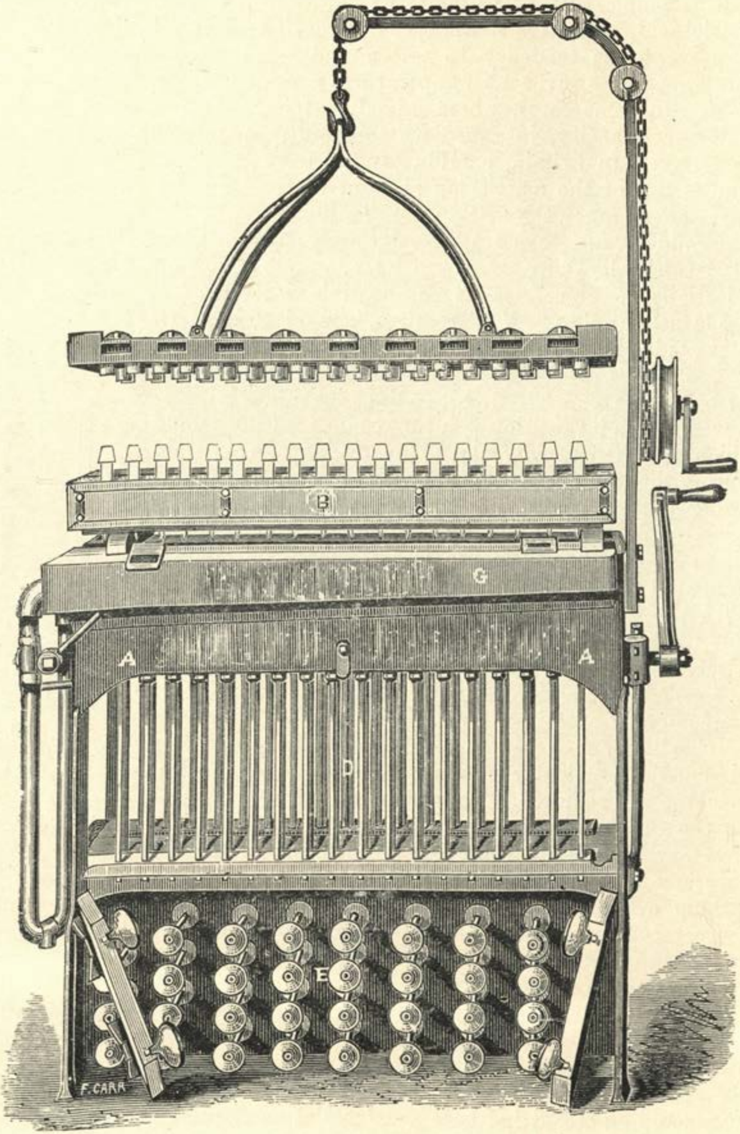

Fig. 137.—Machine for Moulding Self-Fitting Butt-End Candles.

usual way. This arrangement does not permit of the wick being run continuously. After each batch of candles is cast the wicks must be severed, and after removal of the nipping frames and candles the butt mould lowered into position. Each wick is then hooked up through its appropriate butt mould and clamped centrally in the axis of the mould so as to be ready for the next casting. This involves much trouble and delay, besides causing the waste of a short length of wick at each candle end. These objections are obviated by making the butt-end moulds in two halves, separable from one another at will, so as to permit of the candles rising upwards when the half-moulds are apart, but tightly closing together and fitting accurately on the tops of the piston moulds when required; the opening and shutting is simply effected by the motion to or fro of a separate handle. When the moulds are closed, the melted candle material is poured in; after setting,

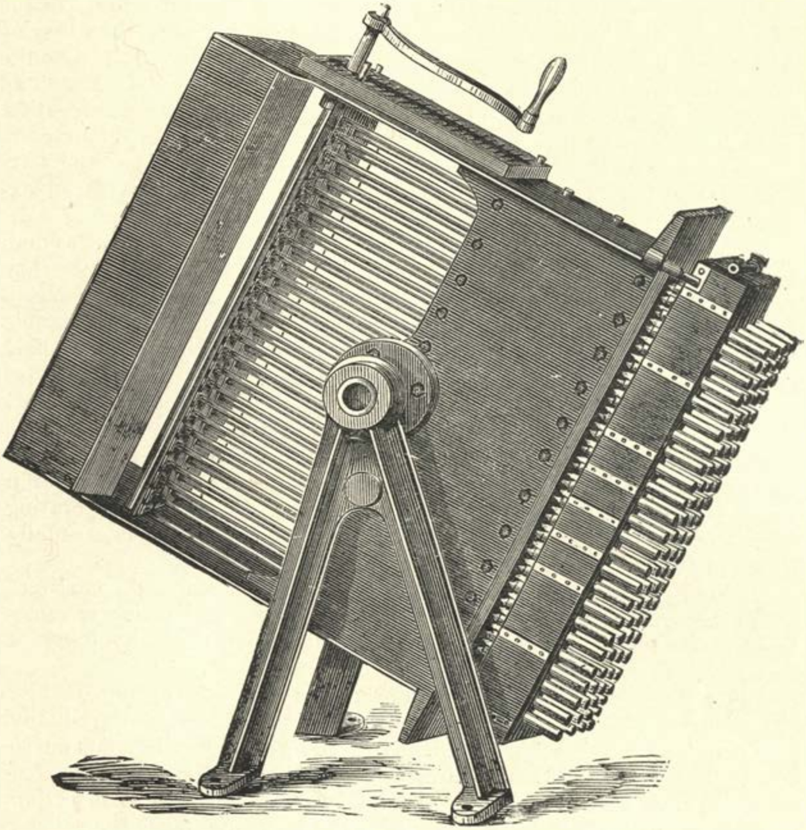

Fig. 138.—Turnover Machine.

this handle is moved back so as to open the butt moulds; the main handle actuating the pistons is then moved so as to raise the candles into the nipping frame; the pistons are next lowered; the butt moulds closed, and a new casting proceeded with.

Candles of Two Materials.—Fig. 138 represents a "turnover" machine, swinging on trunnions, so that when a hard candle material has been run into the moulds and has partly solidified round the sides, the machine can be tipped over so as to allow the still liquid portion of the material in the centre of the moulds to run out, thus leaving hollow candles which are then filled in with softer material. Candles of comparatively easily fusible substance can thus be prepared with an outer casing of less fusible material which prevents the guttering that would otherwise occur.

A process of this description has been patented by *Greig* and *Gardener* (Eng. Pat. 25,397, 1898), the candles being coated with an external shell of combustible material of higher melting point.

Coloured Candles.—Stearine candles are comparatively seldom tinted, being generally burnt uncoloured; sometimes, however, they are tinted a yellowish shade with gamboge, etc. For tinted paraffin candles, however, a considerable demand exists. Formerly the candle material was coloured by incorporating a small quantity of very finely ground pigment; but this is now never done if it can be avoided, as the wick almost invariably becomes clogged after burning a short time, so that a smoky less luminous flame results. Coal-tar dyestuffs are generally preferred, as far as possible free from fixed mineral constituents. In many cases these will not dissolve in pure paraffin wax; but by dissolving them in melted stearic acid, and incorporating a little of the solution with the melted paraffin, the latter can usually be readily tinted to any required depth of shade.

Polishing.—In the case of stearine and wax candles, and sometimes with other varieties also, an extra degree of gloss and polish is sometimes given to the surface by rubbing and rolling them by hand or between cloth-covered rollers, etc.

Several machines have been constructed for this purpose. Fig. 139 indicates a simple arrangement in which the candles are gradually passed out of the tray, A (by means of the grooved roller, B), on to the endless cloth, E D E D, and rolled between the cloth-covered rollers, G G G, and the cloth. The latter moves in such a direction as to carry the candles forward towards the tray, H, whilst the rollers, G G G, revolve in a contrary direction so as to rub and polish the surfaces of the candles. A small circular saw, C, trims the bases of the candles as they emerge from the tray, A. Paraffin candles as a rule are sufficiently smooth and glossy when properly moulded without any additional polishing.

Nightlights.—The use of "mortars," or mortuary candles, for burning in death chambers, etc., is very ancient, wax tapers being the form usually employed until comparatively recently, when the use of short stumpy candles of peculiar composition and construction became general for burning at night under such circumstances that whilst only giving a feeble illumination the flame is required to burn steadily and constantly for a number of hours together.

Two different forms of "nightlights" are now chiefly employed, one set in a case of paper, wood-shaving, or similar material, sufficiently fluid-tight to prevent the melted combustible material from running out; the other cast into shape without any such covering. The wick in each case is generally supported at the base by a "sustainer," consisting either of a little metal disc with a small central perforation through which the wick passes, or a similar small plaster of Paris plate, etc., the object being to prevent the wick from falling over when the light has nearly burnt out so that little or no solid grease is left to support the wick.

The nature of the material burnt varies considerably; for encased nightlights substances are generally chosen the melting points of which are not extremely high, so that the cost is less; while for nightlights of the "pyramid" kind without cases, substances of comparatively high melting points are preferable.

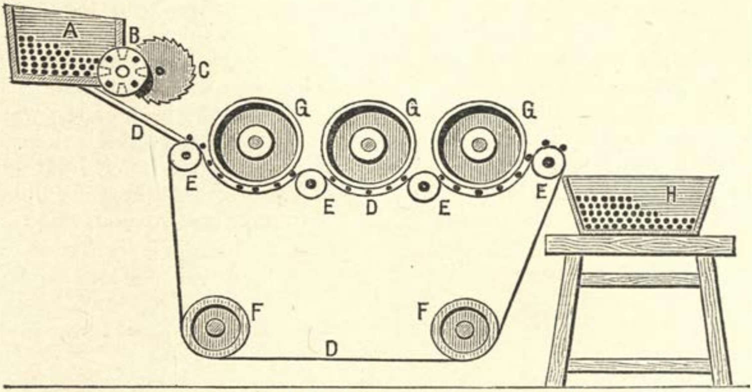

Fig. 139.—Polishing Machine.

Considerable variations are shown in the methods of preparing nightlights. In some instances the pasteboard or wooden case is simply filled up with melted candle material from a can after the bit of wick and "sustainer" are fixed in position by means of a drop of melted grease, applied after the wick has been passed upwards through a minute hole in the bottom of the box. Such nightlights are generally placed in a saucer of water when burnt.

Others are moulded round the wicks in much the same fashion as ordinary longer candles; whilst others are cast as solid cylinders of fatty matter, through the centre of which a hole is perforated. The wick previously threaded on a little bit of tinfoil, is passed upwards through the perforation, and fixed in position sufficiently securely by a blow carefully given with a peculiar kind of hammer; these are generally burnt in glass dishes without water.

Palmitic acid from palm oil, highly pressed coconut stearine, and pressed tallow are the materials most frequently employed as combustible matter. Wicks of rush pith peeled so that two small strips of peel are left adherent on opposite sides are used for some, the effect of the strips being to turn outwards in burning, giving a well-shaped flame.

Spills for lighting candles, etc., are generally drawn by much the same process as that above described for thin wax tapers, the wicks being wound on a drum after passing through the melted composition and a suitable sized draw-plate. After cutting to length the ends are "feathered" by dipping them into hot water sc as to melt half an inch or so of composition and giving them a vigorous shake or jerk which dislodges most of the melted materials, slightly separating strands in so doing.

Medicated Candles.—For the purpose of impregnating the air of sickrooms, etc., with disinfecting vapours, certain substances are sometimes mixed with the candle material—*e.g.*, *iodine* and *eucalyptus oil.* In the latter case the effect is produced by the volatilisation of eucalyptol from the hot cup of melted grease at the base of the wick, that portion which is burnt in the flame being ineffective. In the case of iodine, the free element is evolved from the flame itself, hydriodic acid, if formed, being largely decomposed again by the heat. Sulphur has been used in similar fashion, sulphur dioxide being formed on combustion.

§ 7. The Soap Industry.

CHAPTER XIX.

MATERIALS USED IN THE MANUFACTURE OF SOAP.

FATTY MATTERS AND ALKALIS.

THE raw fatty materials employed in any large quantities for the manufacture of ordinary household soaps and those used for technical purposes, such as wool-scouring, etc., are far less numerous than the different varieties of oleaginous matters used for culinary, edible, and miscellaneous purposes throughout the world in different countries; but almost every day new sources of oily and fatty matters from abroad are brought to light, many of which only require suitable development to furnish excellent material for soap-making as well as for more refined uses.

The leading substances of animal origin in largest use for soap-making are the fats of the sheep and ox (tallow), horse-grease, damaged hog's lard, kitchen grease, and similar materials derived from trade refuse of different kinds (such as tannery, bone-boiling, and glue-making greases), together with seal and whale oils, cod and shark liver oils, fish oils of various kinds, and such-like materials, including sewage grease, egg yolks, and greases recovered from soapsuds, wool washing, engine waste cleansing, etc., and, more recently, hydrogenated oils.

Among the more prominent materials of vegetable origin may be mentioned the oils and butters derived from olives; cotton, sesamé, sunflower, rape, and linseeds; arachis and coconuts; palm fruits and kernels; niger and poppy-seeds; castor beans and almonds; and in less degree a large variety of analogous substances, mostly either the "foots" formed during refining (p. 347), or the inferior qualities, obtained as the last hot pressings, or by treatment with carbon bisulphide and similar solvents, of the partially exhausted mass from which oils of finer quality, suitable for superior applications, have been previously expressed or otherwise obtained; it being a sort of general axiom that any kind of greasy or oleaginous matter can be made into soap of a more or less useful and valuable character even when fit for no other applications, the coarsest kind of cart grease and such-like rough lubricants alone excepted.

A certain amount of higher priced soaps (toilet and special varieties) is also prepared from less coarse fatty matters, in some instances from materials of the finest qualities; but the quantity of these superior grades made bears only a small proportion to the total amount of ordinary coarser soaps manufactured for scouring and laundry purposes (*vide* Chap. xx.).

Alkalis.—The term *alkali* is usually traced to the Arabic *Al kali*, a name applied to a particular plant (a kind of "glass-wort"), the ashes of which abound in potash, and have consequently been used from the earliest ages, not only for the manufacture of glass (whence the English trivial name), but also for laundry and detergent purposes generally. The term "potash," indeed, connotes much the same idea, being originally applied to the soluble part of wood-ashes dissolved out by water and recovered by boiling down the solution in a pot; pearlash being the same material subjected to further purification so as to whiten it. Even at the present day, crude ashes from vegetable substances are often used as a detergent without purification, the earthy and calcareous insoluble matters present serving rather to aid scouring purposes. Thus, cigar ash furnishes a very effective dentifrice.[1]

The difference in character (from the soap boiler's point of view) between the alkali contained in the ashes of inland vegetation (potash) and that present in marine plant ash (soda), appears to have been known to a considerable extent to the alchemists of the earlier and middle ages of the Christian era; although the essential chemical differences between the two, and the practical identity of the latter with the mineral product *natron*, were probably not so clearly understood.

The effect of treatment with quicklime so as to render "mild alkali" (carbonate) "quick" or "caustic," and the superior action of the quickened product on oleaginous matters, so as to form soap, were also more or less imperfectly known to them. At the present day the alkalis used in soap-making are generally (though not invariably) used in the caustic condition because of this more rapid action; but saponification can be effected by carbonated alkalis if sufficient time be allowed, or if the action be accelerated by increased heat and pressure. In all probability the action of an alkaline carbonate essentially consists of the formation of soap and bicarbonate. Thus in the case of stearin and sodium carbonate—

$$\overset{\text{Stearin.}}{C_3H_5(C_{18}H_{35}O_2)_3} + \overset{\text{Sodium Carbonate.}}{3Na_2CO_3} + \overset{\text{Water.}}{3H_2O} = \overset{\text{Glycerol.}}{C_3H_5(OH)_3}$$

$$+ \overset{\text{Sodium Stearate.}}{3Na(C_{18}H_{35}O_2)} + \overset{\text{Sodium Bicarbonate.}}{3NaHCO_3}.$$

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[1] A few years ago an ancient tomb dug up in Rome was found to contain a quantity of what appeared to be ashes, which were appropriated by one of the workmen for his wife to use in washing. It subsequently transpired that the ashes were the remains of the Emperor Galba, who was cremated some eighteen centuries ago (*Times*).

Under the influence of heat the bicarbonate breaks up into carbon dioxide, water, and neutral carbonate, which last then reacts as before—

$$\begin{array}{ccccccc} \text{Sodium Bicarbonate.} & & \text{Sodium Carbonate.} & & \text{Carbon Dioxide.} & & \text{Water.} \\ 2NaHCO_3 & = & Na_2CO_3 & + & CO_2 & + & H_2O. \end{array}$$

Ammonia usually exerts a considerably less energetic saponifying action on most kinds of fatty matters than the fixed alkalis; whilst lime, magnesia, zinc oxide, lead oxide, and similar materials, although useful in the preparation of earthy and metallic soaps for other purposes (candle-making, preparation of lead plasters, etc.), are not used in the direct manufacture of ordinary soaps; excepting in so far as small quantities of lime, iron, and other metallic soaps are often present, as impurities derived from the water or the materials and utensils used, etc.

Formerly the manufacture of alkali, especially soda, was very frequently conjoined with that of soap; but of late years it has become more usual to dissever the two trades, the soap-boiler purchasing either caustic or carbonated alkali from the alkali manufacturer instead of preparing it himself. At one time the chief source of potash was the ashes of terrestrial vegetation (whence the term "vegetable alkali"); but mineral potassium chloride (chiefly from the Stassfurth deposits) is now largely employed as raw material, being converted into potassium carbonate by the Leblanc process.[1]

Similarly, in the earliest ages, soda (*natron*) was derived from saline efflorescences on the soil, whence the term "mineral alkali"; subsequently, the ashes of sea-weeds and marine plants furnished a cheaper source known as "barilla"; whilst latterly, soda produced by the method of Leblanc, or by the more recent "ammonia process" for converting rock-salt into sodium carbonate, has largely superseded all other kinds. By either of these processes, "soda ash" (more or less impure anhydrous sodium carbonate) and "caustic soda" (sodium hydroxide) are prepared in the solid state, the latter being usually put up in air-tight iron drums for transport and preservation. When caustic liquors of a given strength are required, they are readily prepared by simply dissolving a known weight of the solid caustic soda in a given volume of water, and are then ready for use. When, however, sodium carbonate or potassium carbonate is bought, it is necessary to "causticise" the salt before caustic lyes suitable for soap-boiling can be obtained. This process consists of dissolving the carbonated alkali in water, adding lime, and boiling the mixture with continual agitation, so that the calcium hydroxide and alkaline carbonate may react on one another in accordance with the equations—

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[1] Conversion into sulphate by treatment with phuric sulacid, and subsequent heating of the sulphate with small coal and calcium carbonate, so as to form alkali carbonate and calcium sulphide (as "black ash"), separated by dissolving out the former by means of water.

$$\overset{\text{Sodium Carbonate.}}{Na_2CO_3} + \overset{\text{Slaked Lime.}}{CaH_2O_2} = \overset{\text{Sodium Hydroxide.}}{2NaOH} + \overset{\text{Calcium Carbonate.}}{CaCO}$$

$$\overset{\text{Potassium Carbonate.}}{K_2CO_3} + \overset{\text{Calcium Hydroxide.}}{CaH_2O_2} = \overset{\text{Potassium Hydroxide.}}{2KOH} + \overset{\text{Calcium Carbonate.}}{CaCO_2}$$

Causticising Process.—In the earlier days of soap-making the causticising of the alkalis employed was generally effected in the cold; a purer lye being thus obtained from "crude" ashes (rough potashes and "black ash") than when the whole was boiled up together, and then allowed to settle. At the present day this method of treatment is but seldom employed in this country, although still in use on the Continent. In order to carry it out to the best advantage the bottom of the vat is covered with lumps of quicklime, which is slaked with water, and then covered as uniformly as possible with 5 parts of soda ash[1] for every 6 parts of quicklime originally used. Another layer of lime is then added, and a second of soda ash, equal in weight to the lime; then a third layer of lime, and a third of soda ash, equal to the second layer. Water, or weak runnings from a previous batch, is then gradually introduced, and the whole allowed to stand till next day, when the caustic soda lye formed is run off through a cock at the base of the vat into a settling tank. More water is then added and allowed to stand as before, and finally run off, giving a much weaker liquor, which is either mixed with the first, or used for lixiviating another batch. The lime mud is then stirred up with more water, and the final weak liquor thus obtained used with a new batch. Conveniently three (or even four) vats are worked in series, exactly like black ash lixiviating tanks; the second liquor from No. 2 is passed through No. 1, coming out of full strength, being itself obtained as the third liquor from No. 3, which is then exhausted. No. 3, being refilled, then becomes No. 1 of a new series; the former No. 1 becomes the second; and so on, methodically.

Crude Leblanc soda liquors are much less frequently used now than was the case before the ammonia soda process had made much head-way. When carbonated alkali, free from sulphide, is treated (as when ammonia soda ash is employed, or Leblanc soda ash prepared from the "salts" that separate on evaporating the crude liquors obtained on lixiviating black ash), the plant used consists simply of some form of steam vessel, such as an old boiler, provided with an efficient agitator. Lumps of quicklime are added (preferably placed on a grating or enclosed in a sort of cage to keep back hard lumps and stones when the lime disintegrates by slaking), and the whole boiled up for one or more hours until the operation is complete, either under pressure in a closed vessel (whereby a considerable saving of fuel and labour is effected), or by means of wet steam in an open pan.

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[1] Theoretically, 106 parts of Na_2CO_3 are equivalent to 56 parts of CaO; a considerable excess of lime, however, is required to ensure causticising in the cold. For steam boiling in practice 200 parts of soda ash are used per 100 of quicklime.

If, on the other hand, crude black ash liquors be used (impure sodium carbonate, etc., dissolved out from black ash by water, containing sulphide owing to the reaction of sodium carbonate solution on calcium sulphide), or the "red liquors" obtained as mother liquors when the crude black ash liquor is evaporated until "salts" (mostly sodium carbonate) crystallise out during evaporation, the causticising action of lime is conveniently used in conjunction with the oxidising action of a current of air blown into the fluid for the purpose of destroying sulphide by conversion into thiosulphate, sulphite, and sulphate; for which purpose a vessel is employed provided at the base with a large rose jet or spiral tube pierced with holes, or a perforated false bottom, through which the air and steam are blown in together so as to keep the whole in agitation and effect the causticising and oxidation simultaneously.

Finally, the whole is allowed to stand at rest awhile, so that the "lime mud" (calcium carbonate, etc.) may settle, and the clear caustic alkali solution run off or pumped into tanks for storage. These are generally made of boiler plate rivetted together (fig. 140). When intended to hold lye for toilet soap, *Dussauce* recommends that they should be lined with sheet lead to prevent possible discoloration of soap through contact of the lye with iron.

In order to causticise the carbonate thoroughly an excess of lime is desirable; the remaining caustic lime in the lime mud, if of sufficient quantity to be worth saving, may be utilised by boiling up again with a fresh batch of carbonated liquors. After being allowed to settle, the clear liquor is pumped off to another pan, where the causticising is finished with another batch of fresh lime, the mud from which operation is again boiled up with fresh carbonated liquor, and so on alternately. The lime mud resulting from the second treatment with carbonated liquors usually contains too little caustic lime to be worth using a third time; but by boiling up with water the adhering soda solution is in the main washed out, and a weak lye obtained, which can be utilised either to dissolve more carbonated alkali, or for other purposes in the factory.[1]

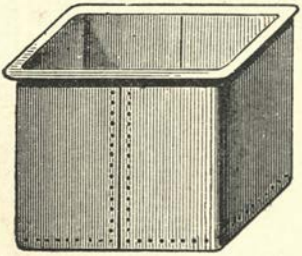

Fig. 140.—Soap Tank for holding Lye.

To causticise sodium carbonate solution thoroughly, the liquor must not be too strong; otherwise a considerable portion of the

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[1] The lime mud finally obtained from soda lyes usually retains a notable proportion of sodium carbonate in a form insoluble in water, chiefly as a double carbonate of calcium and sodium. This may be regained in Leblanc alkali works by drying and using the impure calcium carbonate obtained over again in the black ash operation; but in ordinary soap works, where the residual lime mud is little better than a waste product, the soda thus retained in the lime mud is usually lost.

alkaline carbonate escapes the causticising action of the lime. On the other hand, when the lyes are made too weak, the quantity of salt subsequently required for "salting out" the soap (Chap. XXI.) is increased. When the open pan system is adopted, a sufficiently complete degree of causticising is generally effected by using liquors of such strengths that the lye finally obtained has a specific gravity not exceeding about 1·075 to 1·10 (15° to 20° Tw.), although slightly higher strengths, up to specific gravity 1·11 or 1·125 (22° to 25° Tw.), are sometimes made. By causticising under pressure, considerably stronger lyes may be effectively prepared, provided that the subsidence of the lime mud and the running off of the clear lye is still effected under the same pressure. Thus, with a pressure of 50 lbs. per square inch, caustic lyes up to specific gravity 1·16 to 1·20 (32° to 40° Tw.) may be readily prepared, provided this precaution is adopted; otherwise the reverse action goes on, caustic soda reacting on calcium carbonate so as to reproduce sodium carbonate (*Parnell*).

When more concentrated lyes are required, they are obtained by quickly boiling down the liquid with as little access of air as possible. Weaker lyes are prepared by diluting stronger ones with water, or with the very weak liquors obtained by "washing" the lime mud left after running off the caustic liquor—*i.e.*, by adding water to the mud, boiling up, allowing to settle, running off the weak lye thus obtained, and repeating the operation so as to obtain another batch of still weaker washings.

The storage tanks in which the caustic lyes are kept should be well closed to prevent absorption of carbon dioxide from the air. This is sometimes effected by pouring a layer of paraffin oil or melted paraffin wax on the lye, of course taking the necessary precautions to avoid any hydrocarbon being drawn off with the lye used for making soap. When properly prepared, no visible liberation of bubbles of gas should be noticeable on adding sufficient hydrochloric or other mineral acid to supersaturate the alkali; this serves as a test of completion during the causticising process.

In order to know what quantity of alkali is used for a given operation, the tanks are fitted with gauges; so that if the level is reduced by a given number of inches, for instance, it is known that so many gallons of fluid have been run off. The alkaline strength of the fluid being known, the total weight of alkali present in the fluid run off is then also known. In general it is more convenient to arrange the lye tanks at an elevation (in the upper part of the factory) so as to run off the lyes by gravitation, than to have them in the basement and pump up the lyes to the coppers, although this latter arrangement economises space.

Electrolytic Production of Alkali.—The decomposition of sodium chloride into chlorine and sodium by means of an electric current has of late years received great attention, and numerous processes have been patented for the purpose. Those based upon the decomposition of fused sodium chloride do not appear to have as yet proved commercially satisfactory; but the use of solutions of potassium or sodium chloride has given good results, and caustic alkalis are now manufactured on a large scale in this way in various European countries, including England, and in America.

Two types of electric cells are employed—one in which metallic mercury is employed to combine with the liberated sodium, and the other in which the cell is divided by means of a diaphragm into an anode and cathode department, the liberated metal being converted into hydroxide in the latter.

An interesting *résumé* of the development of this branch of the alkali industry was given by *Swan*.[1]

In a process patented by *Brocket* and *Ranson* (Eng. Pat. 7,397, 1901) the alkali is obtained by the decomposition of an alkali sulphide.

Valuation of Alkalinity of Lyes.—In order to determine the alkaline strength of soap lyes with absolute accuracy, a volumetric assay with a standard acid solution must be employed; but for general soap-making purposes, the specific gravity of the solution is a sufficiently near indication.

It should be borne in mind, however, that the specific gravity is only to be trusted as an indication of alkalinity in cases where the character of the liquor is always sensibly the same—*i.e.*, where the proportion of saline matters other than caustic alkali (sodium or potassium chloride, sulphate, etc.) does not vary much.

This is usually the case when soda ash, etc., of a tolerably uniform quality is always employed; but when different grades are used at different times, lyes may easily be obtained of considerably different alkaline strengths although of the same specific gravity. Thus, if soda ash be used, made by the ammonia process and containing, say, 56 per cent. of "anhydrous soda" ($Na_2O = 62$), equivalent to about 96 per cent. of anyhdrous sodium carbonate, Na_2CO_3, a lye having a given specific gravity (say 1·075) at the ordinary temperature will be notably stronger in alkali, bulk for bulk, than a similar lye prepared from Leblanc soda of, say, 52 per cent., equivalent to about 89 per cent. of anhydrous carbonate, because the latter contains a larger proportion of sodium salts (chloride, sulphate, etc.), which increase the relative density of the liquor without adding to its alkaline strength.

A fortiori, if a "48 per cent. soda ash" (*i.e.*, an ash containing alkali equivalent to only 48 per cent. of Na_2O, equivalent to about 82 per cent. of Na_2CO_3) be used, the alkaline strength of the lye will be lower still for the same specific gravity, since, in order to reduce the alkalinity of the ash to "48 degrees" (48 per cent. Na_2O), an extra amount of some diluting agent (usually salt) must be added.

Similar remarks obviously apply to potash lyes made from potash of different grades, and to caustic soda lyes made by directly dissolving solid caustic soda in water. The lye from a "70 per cent. caustic" (containing 70 per cent. Na_2O = about 90 per cent. NaOH) will usually be stronger, bulk for bulk, at a given specific gravity than that from

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[1] *J. Soc. Chem. Ind.*, 1901, xx., 667.

a "60 per cent. caustic" (containing 60 per cent. Na_2O = about 77 per cent. NaOH), except in so far as the difference in strength between the two kinds of caustic is due simply to *water*, and not to saline matters, such as sulphate and chloride.

The following tables exhibit the relationships between the alkaline strengths of *pure* solutions of sodium and potassium hydroxides and carbonates, and their respective specific gravities, at the ordinary temperature (15° C.), or at more elevated temperatures :—

Specific Gravity of Sodium Hydroxide Solution at 15° *C.* (*Tünnermann*).

Specific Gravity.	Per cent. of Na_2O.	Specific Gravity.	Per cent. of Na_2O.	Specific Gravity.	Per cent. of Na_2O.
1·4285	30·22	1·2912	19·95	1·1428	9·67
1·4193	29·62	1·2843	19·34	1·1330	9·07
1·4101	29·01	1·2775	18·73	1·1233	8·46
1·4011	28·41	1·2708	18·13	1·1137	7·86
1·3923	27·80	1·2642	17·53	1·1042	7·25
1·3836	27·20	1·2578	16·92	1·0948	6·65
1·3751	26·59	1·2515	16·38	1·0855	6·04
1·3668	25·99	1·2453	15·71	1·0764	5·44
1·3586	25·39	1·2392	15·11	1·0675	4·84
1·3505	24·78	1·2280	14·50	1·0587	4·23
1·3426	24·18	1·2178	13·90	1·0500	3·63
1·3349	23·57	1·2058	13·30	1·0414	3·02
1·3273	22·97	1·1948	12·69	1·0330	2·42
1·3198	22·36	1·1841	12·09	1·0246	1·81
1·3143	21·89	1·1734	11·48	1·0163	1·21
1·3125	21·76	1·1630	10·88	1·0081	1·60
1·3053	21·15	1·1528	10·28	1·0040	1·30
1·2982	20·55				

Specific Gravity of Sodium Hydroxide Solution at 15° *C.* (*Lunge and Hurter*).

Specific Gravity.	Grammes of Na_2O per Litre.	Specific Gravity.	Grammes of Na_2O per Litre.	Specific Gravity.	Grammes of Na_2O per Litre.
1·005	3·7	1·170	136·8	1·340	322·2
1·010	7·5	1·180	145·8	1·350	334·4
1·020	15·1	1·190	154·9	1·360	347·2
1·030	22·6	1·200	164·0	1·370	360·1
1·040	30·2	1·210	174·7	1·380	372·9
1·050	37·7	1·220	185·5	1·390	385·7
1·060	45·5	1·230	196·3	1·400	398·5
1·070	53·2	1·240	207·0	1·410	411·8
1·080	61·0	1·250	217·8	1·420	425·0
1·090	68·8	1·260	228·9	1·430	438·2
1·100	76·5	1·270	240·0	1·440	451·4
1·110	84·3	1·280	251·0	1·450	464·6
1·120	92·1	1·290	262·1	1·460	479·9
1·130	100·5	1·300	273·2	1·470	495·3
1·140	109·6	1·310	285·4	1·480	510·6
1·150	118·6	1·320	297·7	1·490	525·9
1·160	127·7	1·330	309·9	1·500	541·2

Influence of Temperature on the Specific Gravity of Sodium Hydroxide Solution.

Temperature.	Specific Gravity.								
Degrees C.									
0	1·015	1·030	1·060	1·100	1·150	1·200	1·250	1·320	1·370
10	1·012	1·027	1·057	1·097	1·146	1·195	1·245	1·315	1·365
20	1·009	1·024	1·054	1·093	1·142	1·190	1·240	1·310	1·360
30	1·007	1·022	1·052	1·091	1·138	1·186	1·235	1·305	1·355
40	1·003	1·018	1·048	1·087	1·136	1·181	1·231	1·299	1·350
50	0·999	1·014	1·044	1·082	1·129	1·177	1·226	1·294	1·345
60	·994	1·009	1·039	1·077	1·124	1·173	1·221	1·288	1·339
70	·988	1·003	1·033	1·071	1·118	1·168	1·216	1·283	1·334
80	·982	·997	1·027	1·065	1·112	1·162	1·211	1·277	1·329
90	·977	·992	1·022	1·059	1·107	1·156	1·206	1·271	1·324
100	·971	·986	1·016	1·053	1·101	1·151	1·200	1·265	1·319

Specific Gravity of Potassium Hydroxide Solution at 15° C.

(Tünnermann).

Specific Gravity.	Percentage of		Specific Gravity.	Percentage of	
	KOH.	K_2O.		KOH.	K_2O.
1·3300	33·69	28·29	1·1437	16·85	14·15
1·3131	32·25	27·16	1·1308	15·50	13·01
1·2966	31·00	26·03	1·1182	14·15	11·88
1·2805	29·65	24·90	1·1059	12·80	10·75
1·2648	28·30	23·76	1·0938	11·46	9·62
1·2493	26·95	22·63	1·0819	10·11	8·49
1·2342	25·61	21·50	1·0703	8·76	7·36
1·2268	24·93	20·94	1·0589	7·41	6·22
1·2122	23·59	19·80	1·0478	5·96	5·00
1·1979	22·24	18·67	1·0369	4·72	3·96
1·1839	20·89	17·54	1·0260	3·67	2·83
1·1702	19·54	16·41	1·0153	2·02	1·70
1·1568	18·20	15·28	1·0050	0·674	0·566

Specific Gravity of Potassium Hydroxide Solution at 15° C. (*Lunge and Hurter*).

Specific Gravity.	Grammes per Litre.		Specific Gravity.	Grammes per Litre.	
	K_2O.	KOH.		K_2O.	KOH.
1·007	7	9	1·252	284	338
1·014	14	17	1·263	297	353
1·022	22	26	1·274	308	368
1·029	30	36	1·285	321	385
1·037	39	46	1·297	335	398
1·045	49	58	1·308	349	416
1·052	57	67	1·320	363	432
1·060	66	78	1·332	377	449
1·067	74	88	1·345	394	469
1·075	83	99	1·357	410	487
1·083	92	109	1·370	425	506
1·091	100	119	1·383	440	522
1·100	111	132	1·397	457	543
1·108	119	143	1·410	472	563
1·116	129	153	1·424	490	582
1·125	140	167	1·438	509	605
1·134	150	178	1·453	530	631
1·142	159	188	1·468	549	655
1·152	170	203	1·483	571	679
1·162	181	216	1·498	593	706
1·171	192	228	1·514	615	731
1·180	203	242	1·530	635	756
1·190	214	255	1·546	655	779
1·200	226	269	1·563	681	811
1·210	237	282	1·580	706	840
1·220	248	295	1·597	731	870
1·231	260	309	1·615	759	902
1·241	272	324	1·634	789	940

Specific Gravity at 15° C. on Sodium Carbonate Solution (*Lunge and Hurter*).

Specific Gravity	Percentage of		Specific Gravity.	Percentage of	
	Na_2O.	Na_2CO_3.		Na_2O.	Na_2CO_3.
1·005	0·28	0·47	1·080	4·42	7·57
1·010	0·56	0·95	1·085	4·70	8·04
1·015	0·84	1·42	1·090	4·97	8·51
1·020	1·11	1·90	1·095	5·24	8·97
1·025	1·39	2·38	1·100	5·52	9·43
1·030	1·67	2·85	1·105	5·79	9·90
1·035	1·95	3·33	1·110	6·06	10·37
1·040	2·22	3·80	1·115	6·33	10·83
1·045	2·50	4·28	1·120	6·61	11·30
1·050	2·78	4·76	1·125	6·88	11·76
1·055	3·06	5·23	1·130	7·15	12·23
1·060	3·34	5·71	1·135	7·42	12·70
1·065	3·61	6·17	1·140	7·70	13·16
1·070	3·88	6·64	1·145	7·97	13·63
1·075	4·16	7·10	1·150	8·24	14·09

Specific Gravity at 30° C. of Concentrated Sodium Carbonate Solution (Lunge and Hurter).

Specific Gravity.	Percentage of		Specific Gravity.	Percentage of	
	Na_2O.	Na_2CO_3.		Na_2O.	Na_2CO_3.
1·140	7·97	13·62	1·230	12·48	21·33
1·150	8·46	14·47	1·240	12·98	22·20
1·160	8·96	15·32	1·250	13·49	23·07
1·170	9·46	16·18	1·260	14·00	23·93
1·180	9·96	17·04	1·270	14·49	24·77
1·190	10·46	17·89	1·280	14·98	25·61
1·200	10·97	18·75	1·290	15·47	26·45
1·210	11·47	19·61	1·300	15·96	27·29
1·220	11·97	20·47	1·310	16·45	28·13

Potassium Carbonate Solutions (Gerlach).

Percentage of K_2CO_3.	Specific Gravity at 15° C.	Percentage of K_2CO_3.	Specific Gravity at 15° C.	Percentage of K_2CO_3.	Specific Gravity at 15° C.
1	1·0091	19	1·1827	37	1·3828
2	1·0183	20	1·1929	38	1·3948
3	1·0274	21	1·2034	39	1·4067
4	1·0366	22	1·2140	40	1·4187
5	1·0457	23	1·2246	41	1·4310
6	1·0551	24	1·2352	42	1·4434
7	1·0645	25	1·2458	43	1·4557
8	1·0740	26	1·2568	44	1·4681
9	1·0834	27	1·2679	45	1·4804
10	1·0928	28	1·2789	46	1·4931
11	1·1026	29	1·2900	47	1·5059
12	1·1124	30	1·3011	48	1·5186
13	1·1222	31	1·3126	49	1·5314
14	1·1320	32	1·3242	50	1·5441
15	1·1418	33	1·3357	51	1·5573
16	1·1520	34	1·3473	52	1·5705
17	1·1622	35	1·3589	52·024	1·57079
18	1·1724	36	1·3708		

The above tables only apply to *pure* solutions of alkaline carbonates and hydroxides. With commercial substances containing other neutral saline matters (chloride, sulphate, etc.) a correction is necessary to allow for the increase in specific gravity brought about by the presence of these impurities without any corresponding increase in alkaline strength. The amount of this correction necessarily varies with the proportion and nature of the saline matter present, and consequently no very accurate allowance on this score is practicable in most cases; but an approximation sufficiently near for most practical purposes is obtained by assuming that the effect of a given quantity of neutral saline matter in increasing the specific gravity is the same as that of the same quantity of actual alkali. Thus, if it is known that a given sample contains *n* per cent. of neutral saline matters, together with $100 - n$ per cent. of actual alkali (reckoned on the sum of alkali and salts as 100), the correction is obtained by subtracting from the tabular number corresponding with the particular specific gravity *n* per cent. of its value. For example, if a solution of sodium carbonate be made from a soda ash, etc., where the saline impurities (sulphate, chloride, etc.) jointly represent 5 per cent. of the total solids dissolved (the sodium carbonate consequently representing 95 per cent.), the amount of sodium carbonate given in the table for a given specific gravity is to be reduced by 5 per cent. of its value. Similarly if the actual caustic soda, NaOH, in a sample of commercial caustic be 90 per cent., and the saline impurities 10 per cent., of the total soluble solid matters present (exclusive of moisture), the tabular number must be decreased by 10 per cent. of its value.

Where more exact valuations are required, as is sometimes necessary in order to avoid using excess or deficiency of alkali, specific gravity indications must be discarded, and the results of alkalimetrical assays substituted for them. For this purpose a normal or semi-normal solution of hydrochloric or sulphuric acid is convenient, used with an indicator not affected by carbon dioxide (litmus employed in hot solution, cochineal, methyl orange, etc.).[1]

English, French, and German Degrees.—By a peculiar trade custom that exists in Britain the alkaline strength of soda ash and caustic soda is represented as higher than the truth to the extent of about 1·32 per cent. or 1 part in 76. This is brought about by the incorrect assumption that the atomic weight of sodium is 24 instead of 23; whence the percentage of Na_2O in pure sodium carbonate, Na_2CO_3, is reckoned as $\frac{64}{108} \times 100 = 59{\cdot}26$, instead of $\frac{62}{106} \times 100 = 58{\cdot}49$. Hence 58·49 parts of soda are reckoned as 59·26, thus giving an error in excess of 0·77 in 58·49 = 1·32 in 100. A still more erroneous mode of calculation was recently current in some districts, based on the same assumption that Na = 24; only in this case the molecular weight of Na_2O was reckoned as 64 instead of 62, thus giving an error in excess of 2 parts in 64 = 3·23 parts in 100, or more than twice the former error.

In Germany the alkaline strength is usually expressed in "degrees" representing the percentage of pure Na_2CO_3 equivalent to the alkali present—*i.e.*, pure sodium carbonate would be a soda ash of 100°.

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[1] When it is required to determine the amount of alkali present in the caustic and in the carbonated state, two estimations are necessary. In one case the total alkali is determined in a given volume of fluid. In the other the same volume of solution is boiled with barium chloride or nitrate, and after cooling, made up to double the original bulk with water; after subsidence or filtration the caustic alkali in half the total fluid is determined, and the amount found doubled and subtracted from that found in the first determination. The difference represents the carbonated alkali with more or less accuracy according as access of carbonate acid from the air has been avoided during the operations.

In France "Descroizilles degrees" are in use, representing the quantity of pure sulphuric acid, H_2SO_4, neutralised by 100 parts of soda ash—*i.e.*, pure sodium carbonate, Na_2CO_3, would represent a product of strength equal to $98 \times \frac{100}{106} = 92{\cdot}45^{\circ}$ Descroizilles. The relationships between Descroizilles and German degrees and the true percentage of anhydrous soda ($Na_2O = 31$, not affected by the above named errors in excess due to English trade customs) are consequently given by the formula—

$$\frac{S}{31} = \frac{D}{49} = \frac{G}{53}$$

where S is the alkaline strength expressed as percentage of Na_2O (equivalent 31—sometimes spoken of as the strength in "Gay Lussac degrees"); D the same in Descroizilles degrees (equivalent of $H_2SO_4 = 49$); and G the same expressed in German degrees (equivalent of $Na_2CO_3 = 53$).

From this formula result the equations—

$$\begin{aligned} S &= \frac{31}{49} D = 0{\cdot}6327\ D \\ &= \frac{31}{53} G = 0{\cdot}5849\ G \\ D &= \frac{49}{31} S = 1{\cdot}5806\ S \\ &= \frac{49}{53} G = 0{\cdot}9245\ G \\ G &= \frac{53}{31} S = 1{\cdot}7097\ S \\ &= \frac{53}{49} D = 1{\cdot}0816\ D \end{aligned}$$

The following table represents the same relationships :—

S.	D.	G.	S.	D.	G.
2	3·16	3·42	42	66·39	71·81
4	6·32	9·84	44	69·55	75·23
6	9·48	10·26	46	72·71	78·66
8	12·64	13·68	48	75·87	82·07
10	15·81	17·10	50	79·03	85·48
12	18·97	20·52	52	82·19	88·90
14	22·13	23·94	54	85·35	92·32
16	25·29	27·36	56	88·52	95·74
18	28·45	30·78	58	91·68	99·16
20	31·61	34·20	60	94·84	102·58
22	34·77	37·62	62	98·00	106·01
24	37·93	41·04	64	101·16	109·43
26	41·09	44·46	66	104·32	112·85
28	44·25	47·88	68	107·48	116·27
30	47·42	51·29	70	110·64	119·69
32	50·88	54·71	72	113·81	123·10
34	53·74	58·13	74	116·97	126·52
36	56·90	61·55	76	120·13	129·94
38	60·06	64·97	77·5	122·50	132·50
40	63·22	68·39			

Calculation of Quantity of Alkaline Lye required for Saponification.—When an alkaline solution of known strength (either determined by titration, or inferred from the specific gravity after correction of the tabular value for saline impurities) is to be used for converting into soap a given kind of fatty matter or mixture of fats, etc., the quantity required for exactly saponifying a given weight of fat depends not only on the alkalinity of the lye but also on the mean saponification equivalent of the fatty matters. The lower the value of this latter quantity the more alkali will be required, the relationship being indicated thus—Let E be the mean saponification equivalent of the fats, etc., used; then E units of weight of fat will be equivalent to 31 units of Na_2O (or to 40 of NaOH, 47·1 of K_2O, or 56·1 of KOH). Let 1,000 parts by weight of alkaline lye be equivalent to a_1 parts of Na_2O (or to a_2 of NaOH, a_3 of K_2O, or a_4 of KOH—*i.e.*, let a_1 (a_2, a_3, or a_4) be the parts per thousand of alkali in the lye. Then E units of weight of fat will obviously be equivalent to $31 \times \frac{1{,}000}{a_1}$ units of weight of lye $\left(\text{or to } 40 \times \frac{1{,}000}{a_2},\ 47{\cdot}1 \times \frac{1{,}000}{a_3}, \text{ or } 56{\cdot}1 \times \frac{1{,}000}{a_4}\right)$; whence one part of fat is equivalent to $31 \times \frac{1{,}000}{a_1} \times \frac{1}{\mathrm{E}} = \frac{31{,}000}{a_1 \times \mathrm{E}}$ parts of lye $\left(\text{or to } \frac{40{,}000}{a_2 \times \mathrm{E}}, \frac{47{,}100}{a_3 \times \mathrm{E}}, \text{ or } \frac{56{,}100}{a_4 \times \mathrm{E}} \text{ parts}\right)$. Thus one part by weight of coconut oil of mean saponification equivalent 215 will be exactly saponified by $\frac{40{,}000}{220 \times 215} = 0{\cdot}846$ part of caustic soda lye containing 220 per mile of NaOH; whilst one part of linseed oil of mean saponification equivalent 291·5 will correspond with $\frac{47{,}100}{150 \times 291{\cdot}5} = 1{\cdot}077$ parts of a potash lye containing total active alkali (caustic + carbonated) equivalent to 150 parts per thousand of K_2O; and so on.

When the alkalinity of the lyes is expressed as *parts by weight per unit of volume* (gramme per litre, pounds per gallon,[1] etc.), the above calculation still applies in slightly modified form. Let the alkaline lye contain b_1 grammes of Na_2O per litre (b_2 grammes of NaOH, b_3 of K_2O, b_4 of KOH), then E grammes of fat are equivalent to $\frac{31}{b_1}$ litres of lye $\left(\text{or to } \frac{40}{b_2}, \frac{47{\cdot}1}{b_3}, \text{ or } \frac{56{\cdot}1}{b_4} \text{ litres}\right)$; whence 1 gramme of fat represents $\frac{31}{b_1 \times \mathrm{E}} \left(\text{or } \frac{40}{b_2 \times \mathrm{E}}, \frac{47{\cdot}1}{b_2 \times \mathrm{E}}, \text{ or } \frac{56{\cdot}1}{b_4 \times \mathrm{E}}\right)$ litres of lye, or 1 kilogramme

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[1] A solution of anything containing *n* grammes per litre (*n* milligrammes per c.c. or *n* kilogrammes per cubic metre), contains *n* pounds per hectogallon (100 gallons), since 1 gallon of water weighs 10 pounds. Hence, when laboratory estimations are made, as usual, on the metrical system, the results can, if required, be referred to pounds and gallons for practical British works' use in a very simple way.

represents $\frac{31,000}{b_1 \times \text{E}} \left(\frac{40.000}{b_2 \times \text{E}}\ \frac{47,100}{b_3 \times \text{E}}, \text{ or } \frac{56,100}{b_4 \times \text{E}}\right)$ litres. Thus, 1 kilo. of coconut oil (E = 215) would be exactly saponified by $\frac{40,000}{200 \times 215} = 0{\cdot}930$ litre of caustic soda solution of such strength that 1 litre = 200 grammes NaHO; or 1 kilo. of linseed oil (E = 291·5) would correspond with $\frac{47,100}{157{\cdot}0 \times 291{\cdot}5} = 1{\cdot}029$ litres of potash lye of which 1 litre = 157·0 grammes K_2O.

The following table gives the values of $\frac{40,000}{\text{E}}$ and $\frac{56,100}{\text{E}}$ for values of E between 190 and 400; by its means the number of litres, x, of caustic soda (or potash) solution can be readily calculated, requisite for the saponification of a kilogramme of any fatty mixture the mean saponification equivalent of which is E, by the simple formula—

$$x = \frac{n}{\text{N}},$$

where n is the tabular number corresponding with E, and N the number of grammes of NaOH (or of KOH) contained in a litre of the lye used :—

E.	$\frac{40,000}{\text{E}}$.	Difference.	$\frac{56,100}{\text{E}}$.	Difference.
190	210·5	..	295·2	..
200	200·0	10·5	280·5	14·7
210	190·5	9·5	267·2	13·3
220	181·8	8·7	255·0	12·2
230	173·9	7·9	243·9	11·1
240	166·7	7·2	233·7	10·2
250	160·0	6·7	224·4	9·3
260	153·8	6·2	215·8	8·6
270	148·1	5·7	207·8	8·0
280	142·8	5·3	200·4	7·4
290	137·9	4·9	193·5	6·9
300	133·3	4·6	187·0	6·5
310	129·0	4·3	181·0	6·0
320	125·0	4·0	175·3	5·7
330	121·2	3·8	170·0	5·3
340	117·6	3·6	165·0	5·0
350	114·3	3·3	160·3	4·7
360	111·1	3·2	155·8	4·5
370	108·1	3·0	151·6	4·2
380	105·3	2·8	147·6	4·0
390	102·6	2·7	143·8	3·8
400	100·0	2·6	140·25	3·55

Thus, suppose a mixture of tallow, palm oil, and coconut oil to have the mean saponification equivalent 250; then $n = 160$, and the number of litres of caustic soda solution required to saponify a kilogramme is $\frac{160\cdot0}{N}$, where N is the number of grammes of NaOH contained in a litre of the lye. If $N = 160$ the quotient is, obviously, 1,000—*i.e.*, 1 litre exactly is required; whilst for stronger and weaker solutions, where N is respectively 320 and 80, the corresponding quotient values are 0·500 and 2·000—*i.e.*, exactly 0·5 litre of the stronger fluid is required, and 2·0 litres of the weaker one.

If the saponification equivalent is not exactly indicated by the table, the value is readily obtained by interpolation by means of the difference columns without introducing any material error. Thus a commercial "oleine" (impure oleic acid) of which the saponification equivalent is 282·5 corresponds with a value for $\frac{40{,}000}{E}$ of $142\cdot8 - (0\cdot25 \times 4\cdot9) = 141\cdot6$; hence, if a soda lye containing 293·6 grammes of NaOH per litre be used ($N = 293\cdot6$), $\frac{141\cdot6}{293\cdot6} = 0\cdot482$ litre of lye will contain alkali exactly corresponding with 1 kilo. of fatty matter.

Obviously, the above formula $x = \frac{n}{N}$ will also afford the data for the calculation of the number of parts by weight of lye required to saponify one part by weight of fatty matter of mean equivalent E, if N denote the parts per thousand of NaOH (or of KOH) in the lye. Thus in one of the examples above quoted, one part of coconut oil of equivalent 215 represents a value for $\frac{40{,}000}{215}$ of $190\cdot5 - (0\cdot5 \times 8\cdot7) = 186\cdot1$; whence the equivalent quantity of soda lye at 220 parts per thousand of NaOH is $\frac{186\cdot1}{220} = 0\cdot846$ part, as before.

When it is required to use fatty matters and alkaline lyes in as nearly as possible equivalent quantities so as to avoid excess of either constituent, calculations such as the foregoing afford the simplest method of arriving at the relative quantities necessary. In practice, when the same kind of operation is to be repeated over and over again as a matter of routine, the fatty matter employed being essentially of the same quality throughout, it usually suffices to gauge the tanks and vessels employed once for all by means of calculations founded on these principles, and preferably checked by careful analyses of the resulting products. The weight of fatty matters taken and their mean saponification equivalent being practically constant for each operation, the volume of alkaline lye used is slightly increased or diminished below that corresponding with the original gaugings according as the alkalimetrical test of the liquor (or the value deduced from its specific gravity) shows that it is a little below or above its normal strength—*i.e.*, that pertaining to the original gaugings.

When it is required to calculate the amount of sodium or potassium hydroxide or carbonate equivalent to a given amount of anhydrous oxide, or *vice versâ*, the following formulæ may be employed, based on the molecular weights—

Na = 23
Na_2O = 62
$NaOH$ = 40
Na_2CO_3 = 106

K = 39·1
K_2O = 94·2
KOH = 56·1
K_2CO_3 = 138·2

Let a given weight A of Na_2O be equivalent to B of $NaOH$ and C of Na_2CO_3; and let a given weight D of K_2O be equivalent to E of KOH and F of K_2CO_3: then—

To reduce	Formula.
$NaOH$ to Na_2O	$A = \frac{62}{2 \times 40} B = 0{\cdot}7750\ B$
Na_2CO_3 to Na_2O	$A = \frac{62}{106} C = 0{\cdot}5849\ C$
Na_2O to $NaOH$	$B = \frac{2 \times 40}{62} A = 1{\cdot}2903\ A$
Na_2CO_3 to $NaOH$	$B = \frac{2 \times 40}{106} C = 0{\cdot}7547\ C$
Na_2O to Na_2CO_3	$C = \frac{106}{62} A = 1{\cdot}7097\ A$
$NaOH$ to Na_2CO_3	$C = \frac{106}{2 \times 40} B = 1{\cdot}3250\ B$
KOH to K_2O	$D = \frac{94{\cdot}2}{2 \times 56{\cdot}1} E = 0{\cdot}8396\ E$
K_2CO_3 to K_2O	$D = \frac{94{\cdot}2}{138{\cdot}2} F = 0{\cdot}6816\ F$
K_2O to KOH	$E = \frac{2 \times 56{\cdot}1}{94{\cdot}2} D = 1{\cdot}1911\ D$
K_2CO_3 to KOH	$E = \frac{2 \times 56{\cdot}1}{138{\cdot}2} F = 0{\cdot}8119\ F$
K_2O to K_2CO_3	$F = \frac{138{\cdot}2}{94{\cdot}2} D = 1{\cdot}4671\ D$
KOH to K_2CO_3	$F = \frac{138{\cdot}2}{2 \times 56{\cdot}1} E = 1{\cdot}2317\ E$

Thus, a solution of sodium hydroxide of specific gravity 1·206 containing 13·3 per cent. of $NaOH$ will contain $13{\cdot}3 \times 0{\cdot}775 = 10{\cdot}3$ per cent. of Na_2O; one containing 21·5 per cent. of K_2CO_3 is equivalent to another containing $21{\cdot}5 \times 0{\cdot}8119 = 17{\cdot}46$ per cent. of KOH; and so on.

The following analogous formulæ may be used to calculate the quantity of soda equivalent to a given weight of potash or *vice versâ*. Let H be a given quantity of sodium carbonate and I the corresponding equivalent of potassium carbonate; similarly let J be a given amount of sodium hydroxide, and K the corresponding potassium hydroxide; and let L be a given quantity of Na_2O, and M the equivalent amount of K_2O. Then—

$$\text{Carbonates, . . .} \left\{\begin{array}{lllll} H & = & \frac{106}{138{\cdot}2}\ I & = & 0{\cdot}7670\ I \\ I & = & \frac{138{\cdot}2}{106}\ H & = & 1{\cdot}3038\ H \end{array}\right.$$

$$\text{Hydroxides, . . .} \left\{\begin{array}{lllll} J & = & \frac{40}{56{\cdot}1}\ K & = & 0{\cdot}7130\ J \\ K & = & \frac{56{\cdot}1}{40}\ J & = & 1{\cdot}4025\ K \end{array}\right.$$

$$\text{Anhydrous Oxides, . .} \left\{\begin{array}{lllll} L & = & \frac{31}{47{\cdot}1}\ M & = & 0{\cdot}6582\ L \\ M & = & \frac{47{\cdot}1}{31}\ L & = & 1{\cdot}5954\ M \end{array}\right.$$

Thus 10 per cent. of K_2O in a given soap is equivalent to $10 \times 0{\cdot}6582 = 6{\cdot}582$ per cent. of Na_2O. A liquor containing 8 per cent. of NaOH is of the same alkaline strength as one containing $8 \times 1{\cdot}4025 = 11{\cdot}22$ per cent. of KOH; and so on.

CHAPTER XX.

SOAP-MAKING PLANT.

HEATING APPLIANCES.

THE plant and appliances required for the manufacture of soap vary somewhat according to the nature of the process used and the scale on which it is conducted. Formerly the vessels (usually known as "pans," "coppers," or "kettles") in which the boiling operations were conducted were uniformly mounted over free fires, so that the flame produced by the combustion of fuel in a fire-place placed beneath the pan was made to play over the rest of the bottom and part of the sides of the pan by means of a suitably arranged circular flue, provided with a damper for the purpose of regulating the draught. Several coppers were usually mounted side by side, so that the products of combustion of their respective fires passed into the same common tunnel or flue leading to the main chimney of the works. At the present day this system of free firing is comparatively seldom applied in the larger soap factories, the coppers being more frequently heated by steam supplied from a special boiler, and in some cases superheated before use. Fig. 141 gives a general idea of the disposition of the

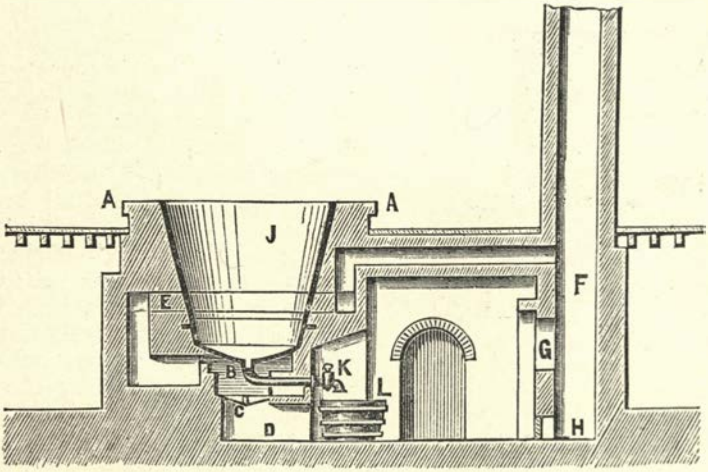

Fig. 141.—Free-Fired Soap Pan.

arrangements adopted for a free-fired pan. The pan, J, is mounted in masonry over the fire-place, B, placed centrally beneath it, a nearly circular flue, E, carrying the flame round the lower part of the pan to the chimney, F; C is the grate or range of firebars supporting the fuel, and D the ashpit. The lyes, etc., are drawn off as required by the tube and draw-off cock, K; the level of the flooring or staging round the pan, A, A, is raised so that the top of the pan projects upwards some 3 feet.

Fig. 142 represents a cast-iron pan of slightly different type, A, also mounted so as to be heated by free firing. In this case the fireplace, B, is not placed centrally beneath the pan, but somewhat in front of it, the heating being chiefly effected by the hot air chamber, E, in which the products of combustion circulate round and under the base of the pan before passing away to the flue. C represents the firebars; D, the ashpit.

In the case of modern steam-heated pans, the steam is applied in various ways. Heating by "*wet*" *steam* consists in blowing steam at a sufficient pressure directly into the mass to be heated, so that the water produced by the condensation of the steam dilutes the whole until the temperature rises so high that the steam simply blows through without becoming materially condensed. For most general boiling purposes a *wet steam coil* is thus used, consisting of an iron pipe descending nearly to the bottom of the copper and terminating in a ring perforated with holes through which the steam issues, bubbling up and producing a very effective agitation and intermixture of the contents when the heat is sufficient to cause the steam to blow through the mass. In some districts this wet steam coil is accordingly spoken of as the "blowpipe." Superheated steam is sometimes employed instead of steam supplied directly from the boiler, so as to diminish the amount of water condensation.

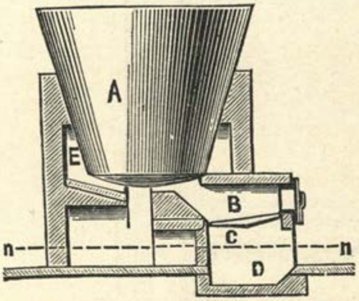

Fig. 142.—Another Form of Soap Pan (Free-fired).

Heating by "dry" steam consists in causing steam (either directly from a high-pressure boiler, or preferably for many purposes, superheated) to circulate through a sort of spiral tube or coil arranged in the lower part of the copper. The water condensed in the coil accordingly does not pass into the heated mass, thereby diluting the lyes, etc., but is blown off together with the exit steam.

Dry steam is also sometimes employed to heat an external jacket usually only surrounding the lower part of the pan. Fig. 143 indicates the kind of arrangement—C, steam supply pipe; D, pipe and cock for drawing off condensed water; A, copper; B, steam jacket at base of copper; E, draw-off pipe from copper. A mechanical stirring arrangement to keep the mass agitated is conveniently added.

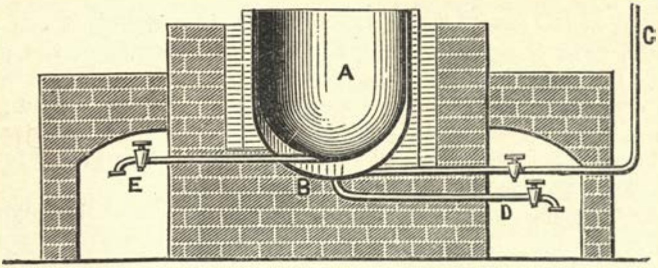

Fig. 143.—Steam-Heated Pan.

In order to facilitate intermixture of materials in the pan whilst heating up by dry steam an appliance known as "Morfit's steam twirl" is much used. Fig. 144 represents one form of arrangement applied

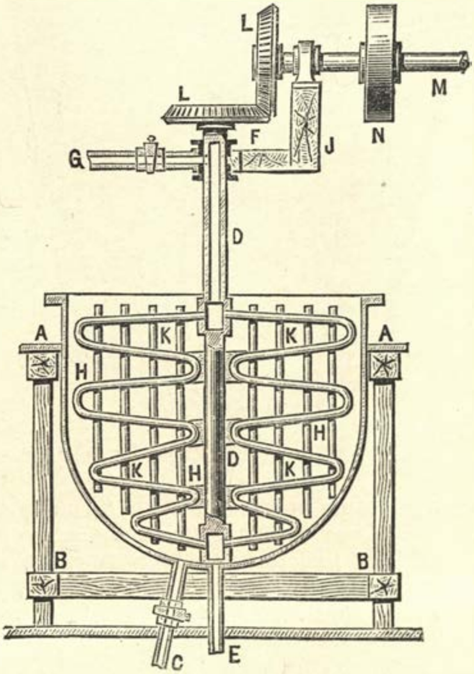

Fig. 144.—Morfit's Steam Twirl.

to a comparatively shallow copper supported by a wooden frame work, A A, B B. The steam from the steam pipe, G, passes into a hollow spindle, D D E, the central part of which is blocked, so that the steam is obliged to pass through the convoluted tubes, K K, K K, braced together by cross pieces, H H H, which also serve as stirring vanes. By means of the bevel wheels, L L, worked from the shaft and pulley, M N, the twirl is set in motion, so that the contents of the pan are thoroughly agitated whilst being heated up. The condensed water is blown off at E with the surplus steam, whilst C is the discharge cock of the pan. The same appliance can also be used with wet steam, the convoluted tubes being pierced with holes so as to allow part of the steam to escape directly into the mass of material.

Soap Coppers.—Formerly the vessels in which soap and lyes were boiled together were made of various kinds of materials; sometimes of masonry, iron bottoms being provided for heating by free fire; sometimes of cast iron, like the pan represented in Fig. 142, or of wrought-iron plates riveted together subsequently, or of wooden staves strongly bound together like enormous tubs, wet steam being the source of heat.

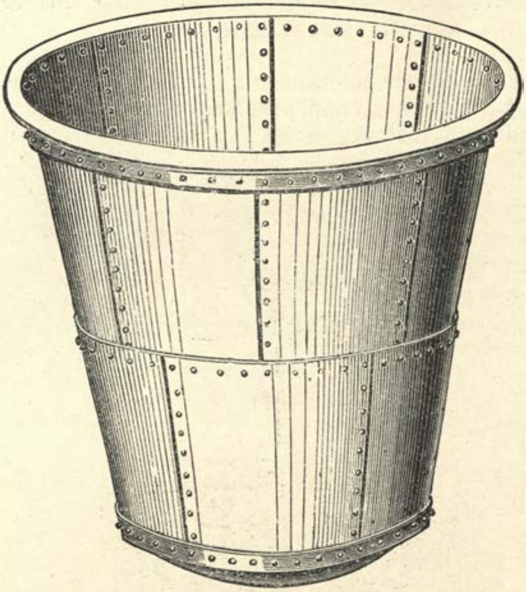

Fig. 145.—Soap Copper.

These forms, however, were, for the most part, adapted only for use with quantities of material small in comparison with those in use at the present day, when charges of 30 to 40 tons and upwards of fatty matters are not uncommon. A more recent form of soap kettle is a cylindrical or conical cauldron with somewhat rounded apex, placed base upwards, and constructed of boiler plates well riveted together, as indicated in Fig. 145. The degree of slope of the sides (regulating the ratio between the top and bottom diameters) and the relation between the depth and maximum diameters vary somewhat in different countries—*e.g.*, soap kettles of this pattern in America are generally from two to three times as deep as they are wide, sometimes filling a building of two or three stories; whilst in Britain the depth rarely exceeds once and a half times the diameter, still shallower pans being often used. A copper 15 feet in diameter and 15 feet deep will turn out 20 to 30 tons of soap, a usual rule being to allow 6 cubic feet capacity (about 37·5 gallons) for each 100 lbs. weight of fatty matters treated, or about 135 cubic feet (nearly 850 gallons) per ton; so that a copper holding some 2,500 cubic feet (upwards of 15,000 gallons) will suffice for about 18 tons of fatty matters yielding 25 to 30 tons of soap according to the amount of water contained therein.

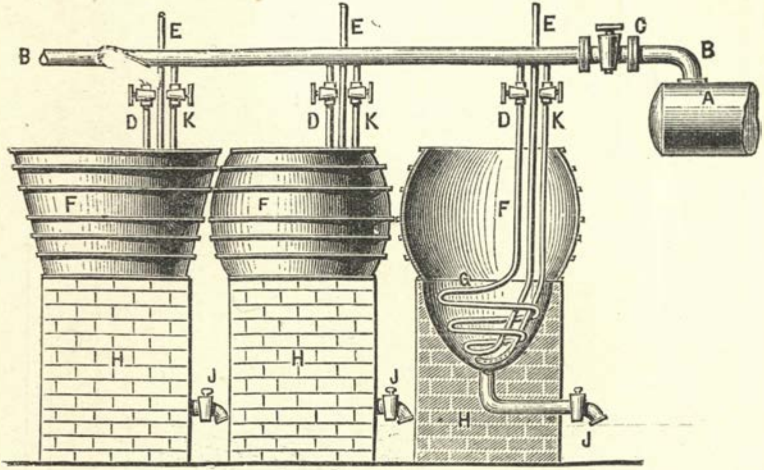

Fig. 146.—Morfit's Steam Series.

Fig. 146 represents "Morfit's Steam Series," a set of three coppers supplied with both sets of steam coils (wet and dry). B B is the steam main supplied from the boiler, A; K is the wet steam pipe; and D F G the dry steam coil. The lowest part of the copper is usually provided with a narrower basin or hat-shaped downward prolongation for the more easy collection and separation of watery lyes, etc.; in the figure it is represented as connected with a draw-off tube, H, provided with a cock, J. F F F represent "Curbs" (*infra*) of different shapes to prevent the liquid boiling over.

Figs. 147 and 148 represent a form of pan for heating with either dry or wet steam as required, constructed by Messrs. W. Neill & Son, of St. Helens, Lancashire. This is a square tank made of steel plates riveted together, with rounded corners and dished bottom, the square form being preferably employed as taking up less room than the circular shape required in the case of free-fired coppers provided with flues running round the lower part of the pan (Fig. 141). The pan is fitted with wet and dry steam coils, and a cock at the bottom for running off spent lyes. A " skimmer pipe " is provided, working on a swivel joint, and capable of being adjusted at any required height by a supporting chain; as represented in the figure, the fluid soap is run off

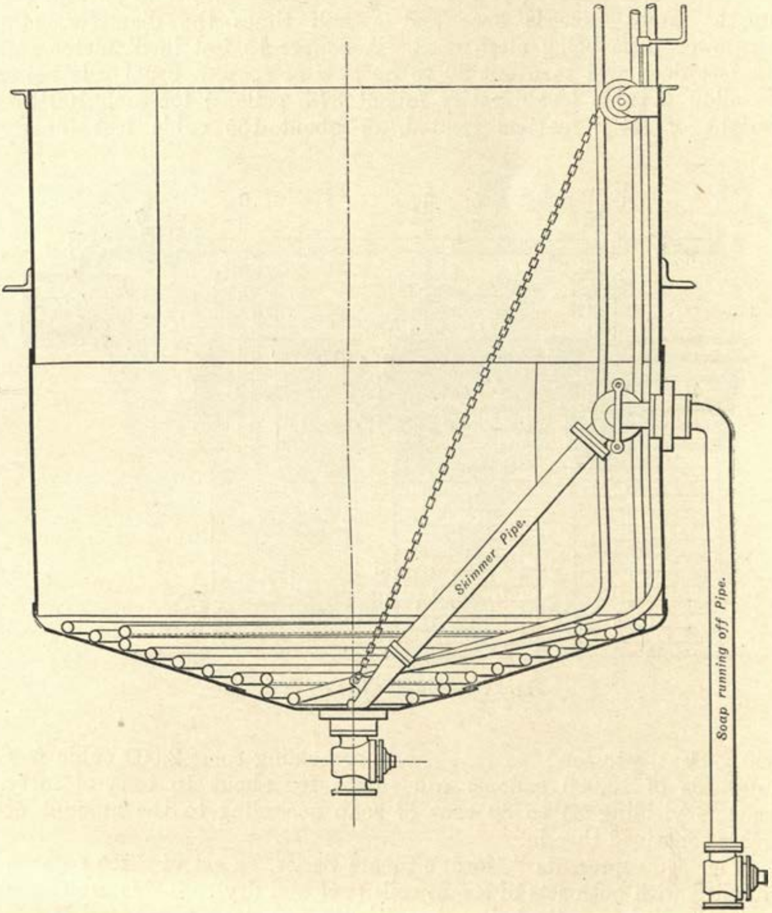

Fig. 147.—Elevation of Steam-Heated Pan.

by gravity through a down pipe; but, if required, a pump can be connected at the elbow instead, a cock being affixed to shut off connection when the pump is not at work.

An air-blast has been employed by *Dunn* for the purpose of intermixing the lye and fatty matters during the preliminary stage of "killing the goods," and the subsequent operations when free-fired pans are employed, with the result that tumultuous boiling was to a large extent avoided. The air was introduced by a "blowpipe" arranged in much the same way as the more modern wet steam coil. The process was said to answer well, but has nowadays fallen into disuse through the substitution of steam-heated pans for free-fired kettles.

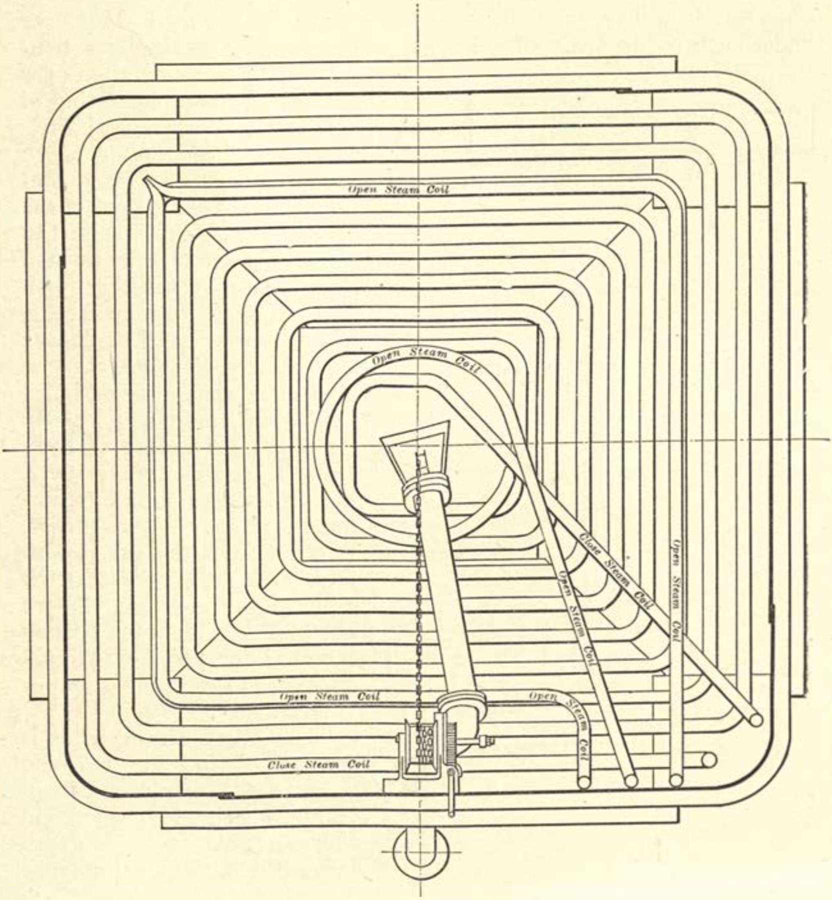

Fig. 148.—Plan of Steam-Heated Pan.

Curb and Fan.—With certain kinds of materials, and particularly at certain stages of the operation, tumultuous boiling up or "bumping," and vigorous frothing are apt to occur, more especially when oleine soap is made by the direct addition of hot carbonated lyes to free oleic acid (red oils, *vide* Chap. XVII.), and during the "graining" or "cutting" of boiled soaps—*i.e.*, the throwing them out of aqueous solutions by addition of salt (*vide* Chap. XXI.). Two appliances are of considerable utility in diminishing the chance of loss by boiling over under such conditions. One, known as the "curb," is simply a temporary expansion of the upper part of the pan, consisting of a conical, circular, or barrel-shaped addition bolted on so as virtually to amplify considerably the dimensions of the copper at the top. Fig. 146 represents a cone, F, of wooden staves, hooped together with iron, applied to one kettle, and a barrel-shaped analogous curb applied to another.

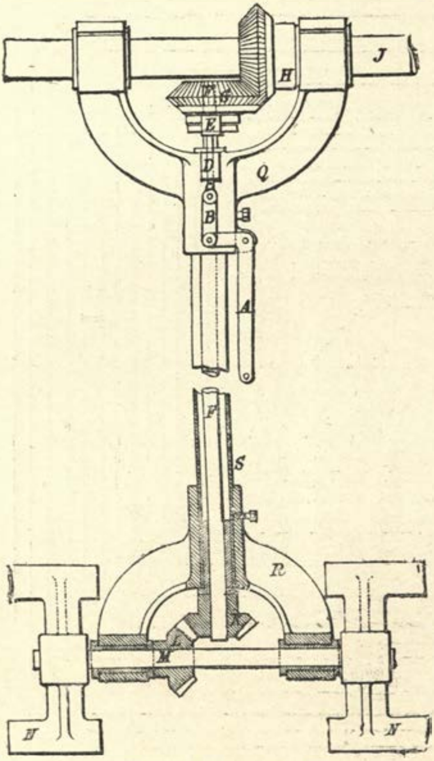

Fig. 149.—Fan.

In an apparatus designed by *Erfurth*, more particularly for the manufacture of rosin soap (Eng. Pat. 5,817, 1901), the froth rises into a scumming chamber above the boiler, where it loses the gas it contains and falls back through a pipe into the boiler. Means are also provided for cooling the chamber and for the condensation of escaping steam or vapour.

The other arrangement is termed a "fan," Fig. 149, and consists of a pair of a sort of paddle-wheels suspended in the pan at such a depth below the surface as may be necessary, so that as the paddles revolve the froth is broken by them and prevented from rising up and boiling over. Motion is communicated to the paddles by means of a vertical shaft with bevel wheels at top and bottom, the shaft being telescopic so as to admit of being drawn up and down to adjust the level of the paddles as required. It rotates within a tube carrying a Y-shaped frame at each end, the whole being suspended from the upper horizontal shaft, by means of which motion is communicated to the vertical shaft through the bevel wheels, whilst the lower Y serves as bearings for the axle of the paddles.

Saponification Under Pressure.—In the saponification process patented by *Haywood* (Eng. Pat. 16,746, 1896), the charge of melted fat and lye is introduced into a horizontal cylinder where it is mechanically agitated, whilst steam is admitted at a pressure of 40 to 60 lbs. It is claimed that by this means the saponification is complete in a few minutes.

A special apparatus intended for the manufacture of resinous soap has been devised by *Arledter* (Eng. Pat. 2,822, 1899). It consists of a closed boiler, surrounded halfway up by a steam jacket, and provided with a false bottom. Water is introduced nearly up to this bottom on which is placed the alkali. Steam is then blown in until the alkali has dissolved, after which the rosin is introduced, and full steam turned on. Finally, the mass is forced by the steam pressure through a filter heated by means of a steam jacket.

Apparatus for Electrolytic Saponification.—Several patents have been taken out for processes and apparatus for using an electric current in saponification.

That designed by *Shee* (Eng. Pat. 22,129, 1897), consists of a conical-shaped trough, provided with perforated agitator-blades revolving on a central spindle. The soda lye is placed in vessels of porous material above the trough, so that their bottoms are brushed by wire brushes fixed to the upper agitator-blades. Within these vessels are placed iron plates forming the positive pole, whilst the spindle is connected with the negative pole.

The oil introduced into the trough is kept at a temperature of 90° to 100° C., and continually agitated, whilst a current of 2 to 4 volts and 100 amperes per cubic metre of fat is passed through it. A neutral soap is formed within seven hours, and where excess of alkali is required for the saponification this excess can be removed by reversing the current.

In another apparatus patented by *Merry* and *Noble* (Eng. Pat. 2,372, 1900), a solution of an alkali salt is electrolysed, and the liberated alkali received in an emulsion of fat with water.

The electrolyte (solution of the salt) and the anode are contained in a porous cell, whilst the cathode, consisting of pervious material, such as wire gauze, surrounds the porous cell. This cell is suspended in the contents of the soap pan, which are kept in motion by a current of steam or air. Means are also provided for collecting the hydrogen, and for circulating and renewing the electrolyte.

Soap Frames.—When the operation of soap-making is finished, and the spent lyes (when such are present) removed by subsidence, etc., the resulting soap usually forms a hot semi-fluid or pasty mass, which, on cooling, more or less thoroughly solidifies to a soft solid substance. In order to facilitate the operation of cutting up the mass into bars and tablets for sale without waste the hot soap is run by gravitation, or ladled, or pumped out of the copper in which it is made into "frames," in which it is allowed to solidify.

The pumps used for this purpose are generally of somewhat different construction from the ordinary suction pump used for wells, etc. Fig. 150 represents a rotary soap pump as constructed by Hersee Brothers of Boston. Instead of pumping out the soap, it may more conveniently be run off by gravity by means of the adjustable "skimmer pipe" shown in Fig. 147, the frames being arranged so that their tops are at a level below the elbow joint of the pipe.

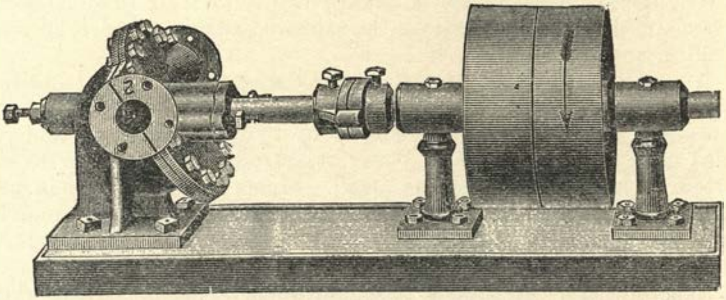

Fig. 150.—Rotary Soap Pump

A method sometimes used for emptying kettles and raising their contents to a higher elevation was introduced by *Gossage*. This consists in the application of a cover fitting air-tight, and then forcing in compressed air, so as to press the semi-fluid soap up a pipe, the lower end of which dips into the kettle to the required depth; the whole arrangement working on the principle of the "acid egg" used in vitriol factories for elevating the acid without employing ordinary pumps.

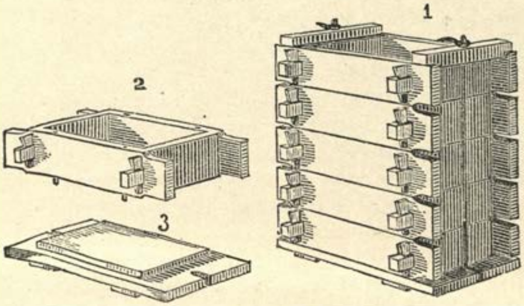

Fig. 151.—Method of Building up Wooden Frames.

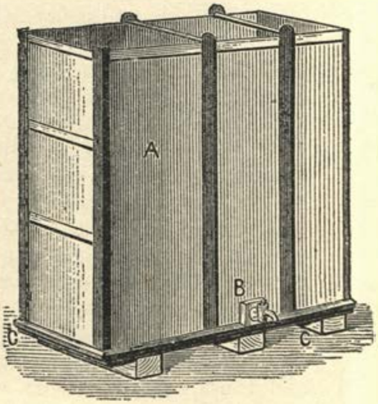

Fig. 152.—Galvanised Iron Frames.

The size of the frames employed and the material of which they are composed vary, wood being preferable when slow cooling is essential,

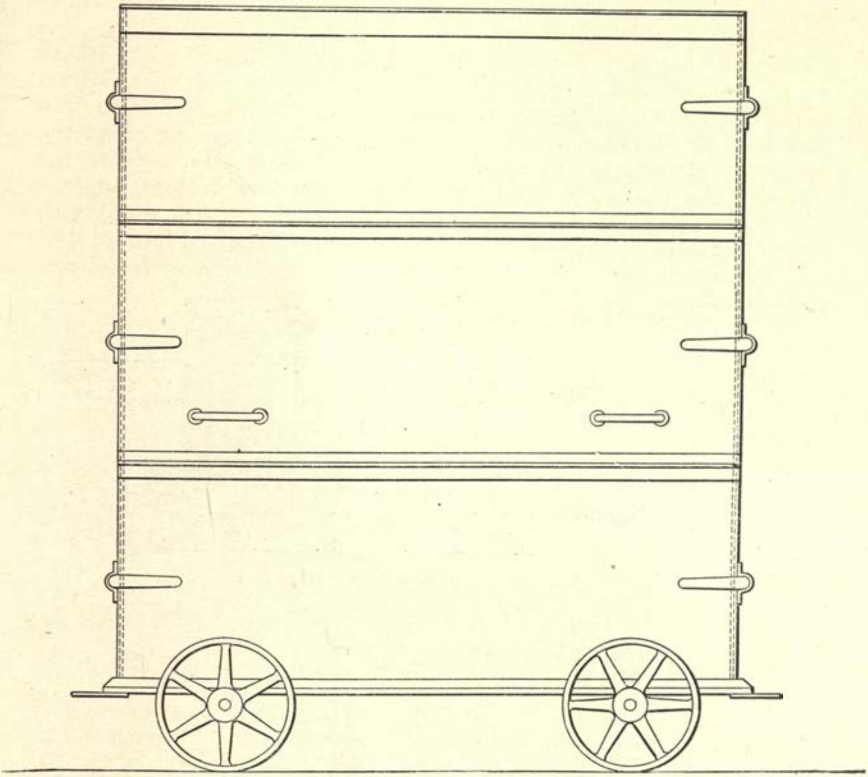

Fig. 153.

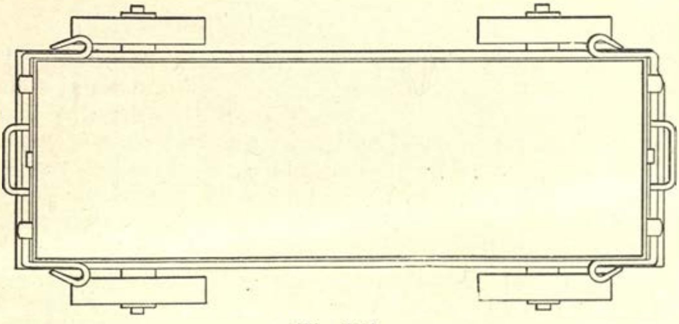

Fig. 154.

Figs 153 and 154.—Improved Form of Steel Soap Frame but iron being considerably more convenient in other cases. For toilet soaps, frames holding 1 cwt. or less are often employed; for scouring soaps much larger ones, furnishing ultimately a block of cooled soap weighing 8, 10, 15, or more cwts.[1]

Fig. 151 indicates the way in which a wooden frame may be built up of a set of squares pegged together and superposed on a bottom board. Fig. 152 represents a frame constructed of galvanised iron plates where the ends fit into grooves formed by turning round the corners of the side plates, or fitting pieces of angle iron thereto; the side and end plates are similarly fitted to the iron bottom, and the whole kept together by two transverse rods at the top fitted with screws and nuts. Figs. 153 and 154 represent an improved form of steel soap frame, mounted on four wheels, and held together by cap fastenings.

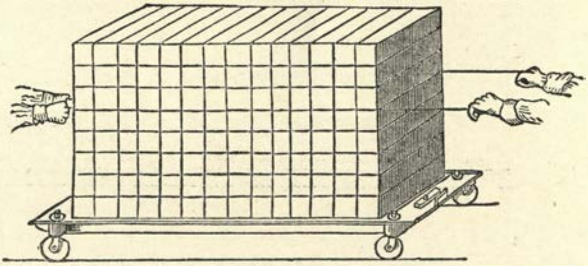

Fig. 155.—Cutting Soap.

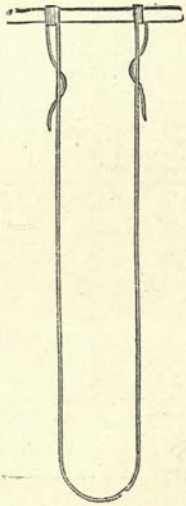

Fig. 156. — Looped Wire for Cutting Soap.

Fig. 157.—Scribe.

When the block of soap has completely cooled down and set solid, the frame is taken to pieces and the block cut into slabs, which are then transversely cut up into bars. When this is dône by hand the block is cut in a very simple fashion by simply pulling a looped wire (figs. 155 and 156) through it horizontally, so as to cut through the mass along a series of parallel lines previously marked on the outside by means of a scribe (fig. 157). Slabbing and barring machines of various patterns are frequently employed for this purpose (fig. 158).

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[1] Formerly, the size of the soap frames was fixed by excise laws and regulations, and required to be 45 inches long by 15 wide, inside measurement, and not less than 45 inches deep (usually made 50 to 60 inches deep), so as to hold some 15 to 20 cubic feet, or about 9 to 11 cwts. of soap. Although no longer compulsory, this size is still largely employed.

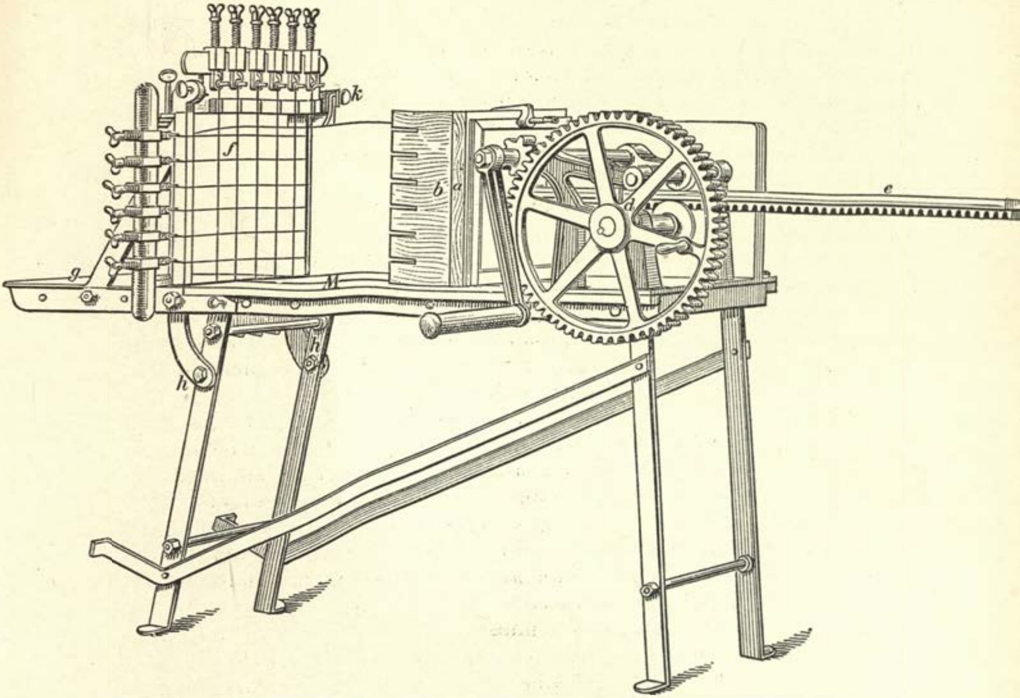

Fig. 158.—Slabbing and Barring Machine.

When it is required that the soap should cool very slowly in the frame (*e.g.*, in order to promote saponification in making cold process soap, or to facilitate mottling—Chap. xx.) the sides of the frame are sometimes padded to keep in the heat (fig. 159).

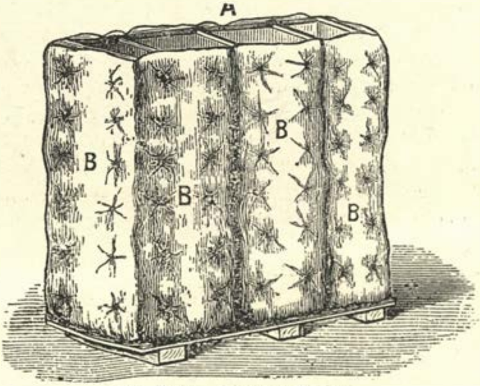

Fig. 159.—Padded Frame.

A frame patented by *Hadfield* (Eng. Pat. 19,903, 1896) is cast in sections and provided with a false bottom, which can be raised by means of chains, hydraulic power, etc. On raising this bottom, the block of soap comes into contact with an arrangement of cutting wires, whilst another cutting frame with horizontal movement completes the division into bars, when the soap has been raised to a sufficient height.

The bars of soap into which a block is cut generally weigh about 3 lbs. They are usually stacked in a hollow pile to dry the outside slightly so as to case-harden them, as it were, or else are stored on lattice-work shelves in an open rack, allowing free access of air.

With very moist soaps, this drying action is apt to go too far, warping the bar out of shape, besides causing it to lose largely in weight. Accordingly such bars are often "pickled" by immersion in brine, which slightly indurates the outside.

Of late years a considerable demand has sprung up for 1-lb. blocks instead of 3-lb. bars.; such blocks are generally cut to size and shape and then stamped like toilet cakes in similar machines but of larger size. Often the block is grooved in the centre, so that it can be readily broken into two; or three grooves are stamped at equi-distant intervals enabling four 4-oz. blocks to be obtained.

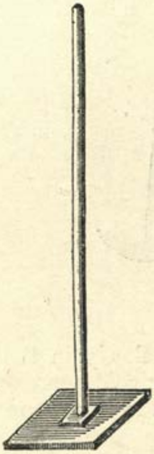

Fig. 160.
Hand Crutch.

Crutching Machines.—Formerly, when it was necessary to stir up soap containing excess of water in the cooling frames to prevent its separating into two liquids, a peculiar hand-worked agitator termed a "crutch" was largely used, consisting of a square piece of board with a handle attached to the centre of the square perpendicular to its plane (fig. 160). By plunging this into the pasty mass, and working it up and down, a sufficiently efficient mixing was brought about.

Such implements are still in use, especially for operations on a small scale, but have been largely superseded by mixing machines, the operation of agitation by their means being still spoken of as "crutching." For intermixing silicate or resinate of soda solution with boiled soaps in large quantities at a time, or for otherwise working in saline solutions to dilute and harden the soap or improve its detergent qualities, or "filling" of various kinds, as well as for preventing separation of watery fluid from the mass, such machines are largely employed.

Steam-Jacketed Crutching Pot.—A steam-jacketed crutching pot is shown in Fig. 161. It has an inner pan of cast iron, and a jacket of mild steel plate. The agitator is in the form of a steel-bladed screw revolving round a fixed wheel, and being provided with a reverse motion effects thorough admixture of the contents of the vessel. A scraper is made to act upon the whole of the interior of the pot, and

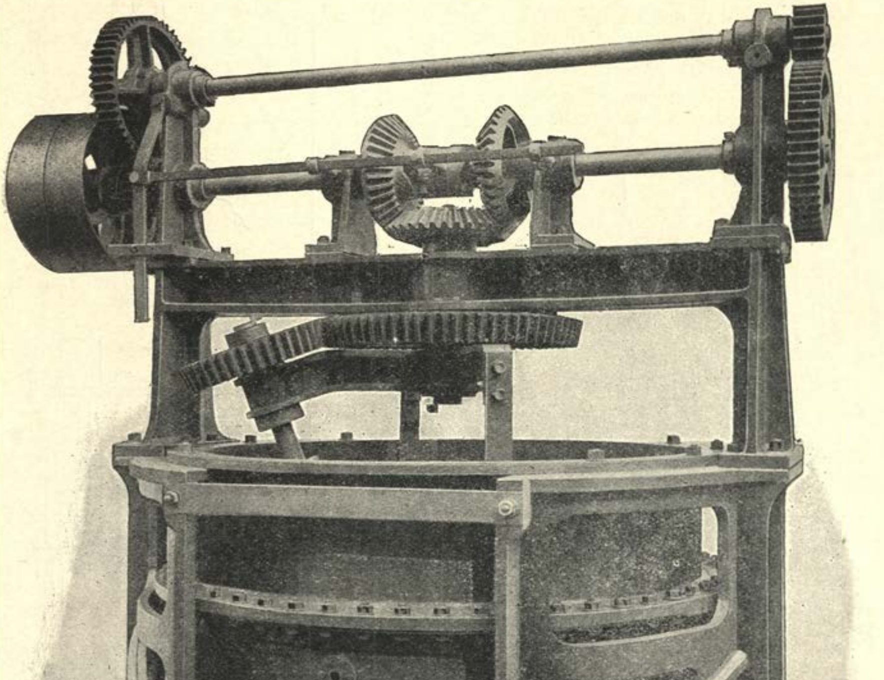

Fig. 161.—Steam-Jacketed Crutching Pot, with Revolving Screw Agitator and Reversing Gear.

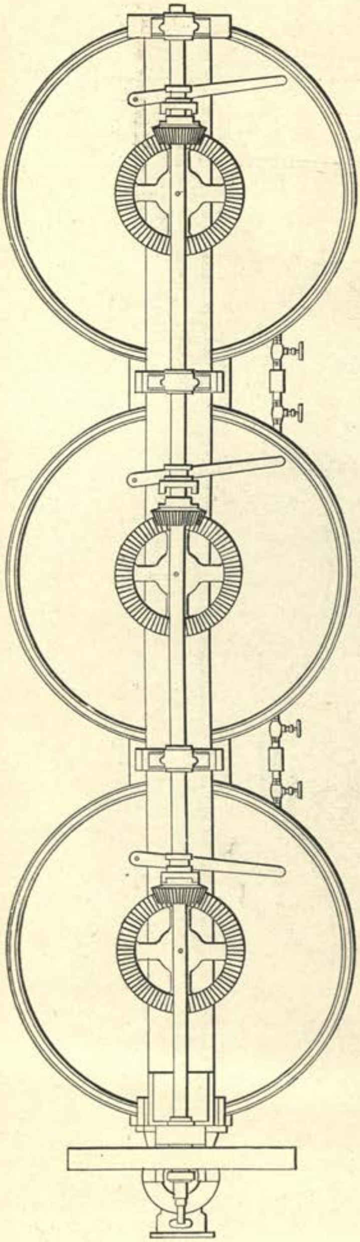

Fig. 162.

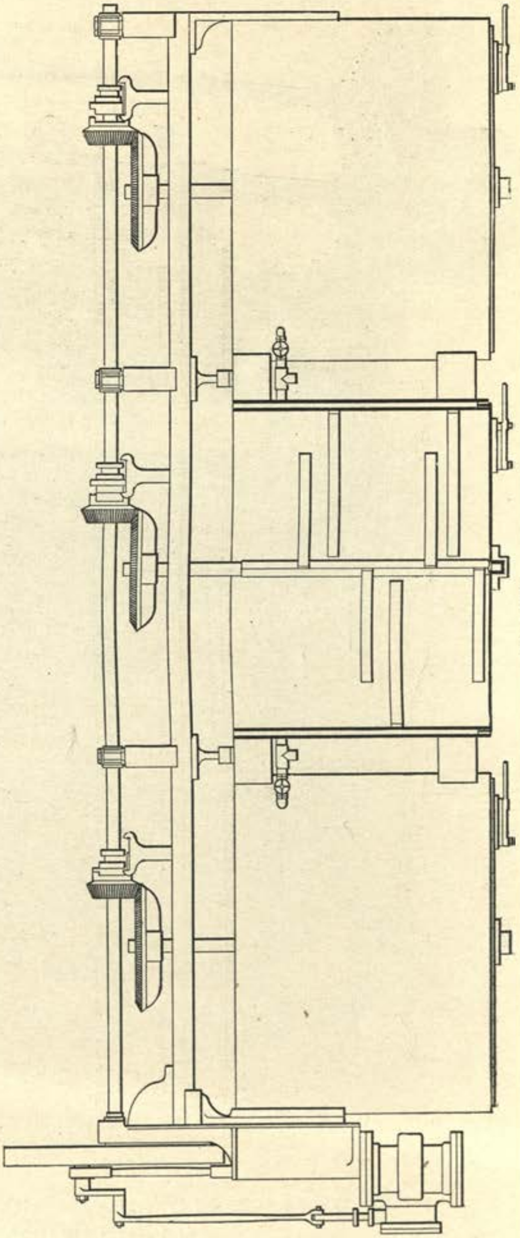

Fig. 163.

Figs. 162 and 163.—Series of Crutching Pans.

there is an outlet valve at the bottom. As shown in the illustration, the apparatus is mounted on two stands.

Figs. 162 and 163 represent a series of three crutching pans arranged so as to be worked from the same shaft. By means of the clutches indicated, any one of the three can be set in motion or stopped as required. The stirring vanes are here horizontal, projecting from a vertical axle, whilst similar fixed vanes are arranged internally so as to prevent the liquid mass from simply swinging round and round without being broken up and intermixed.

In another form of mixing machine two sets of vanes are provided, moved in opposite directions by means of bevel wheels, one axle being hollow and the other working inside it like the axles carrying the two hands of a watch. The vanes slope at an angle of 45°, so that the material is continually lifted and the different layers intermixed, the general action resembling that of an ordinary egg-whisk. Large steam-driven sizes are very effective; but if worked too rapidly the mass is apt to become frothy. For very stiff soap, an archimedean screw, working inside a wider cylinder, answers very well.

Toilet Soap Machinery.—In the manufacture of various kinds of toilet soaps, special appliances are used varying in their nature with the process adopted. When "stock" soaps prepared on the large scale are "re-melted," for the purpose of blending together different kinds, with the addition of colouring or scenting materials, etc., a steam-jacketed pan is generally preferred, constructed somewhat after the fashion of fig. 143. As the soap (previously cut up into small lumps) melts, it is mixed together either by hand-crutching (*supra*) or by means of some form of agitator. In the latter case too rapid a movement must not be communicated, since otherwise air bubbles are stirred in, and the soap becomes more or less frothy, forming a spongy mass when solid.[1] Figs. 164 and 165 represent a very effective form of re-melter constructed by W. Neill & Son, where the heating action of the outer steam jacket is greatly amplified by means of the internal cross steam pipes. The pieces of soap are continually brought in contact with these by the motion of the agitating arms, and as a large heating surface is thus brought into play, the re-melting proceeds rapidly.

After the intermixture of the various ingredients intended to render the soap emollient, to scent it, or otherwise to improve its qualities, the fluid mass is cast in small frames so as to form blocks of ½ cwt. or upwards, according to circumstances. As a rule, these are made of iron plates bolted together, as indicated in fig. 152, so as to cool quickly and avoid, as far as possible, loss of volatile scenting materials, and the injurious effect of heat thereon.

The blocks, when cold, are slabbed and barred by hand or machine, and the bars cut into short lengths, each of which is then stamped

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[1] "Floating" soaps are purposely prepared in this way, enough air bubbles being worked in to enable the tablet to float in water, even after compression in the stamping press.

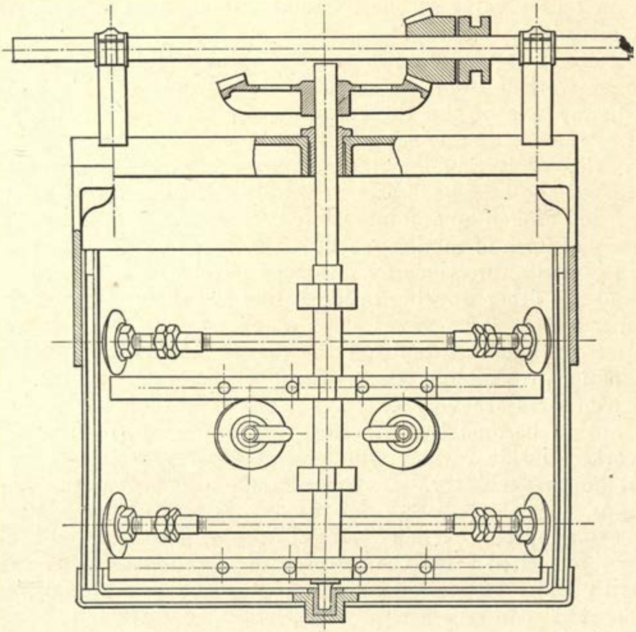

Fig. 164.

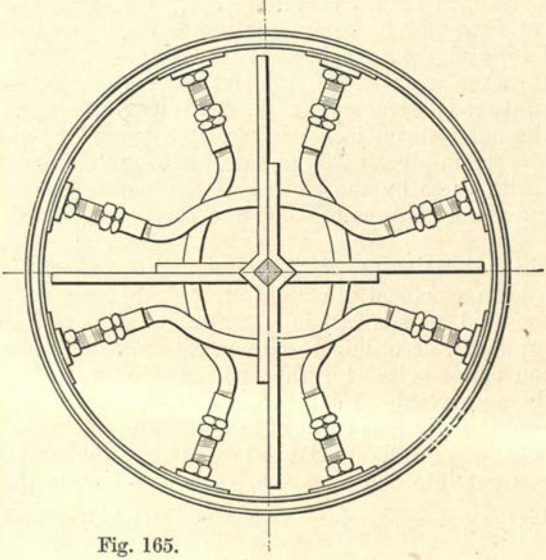

Fig. 165.

Figs. 164 and 165.—Neill & Son's Re-melter.

into tablet form by some form of press acting on the principle of a coining press, where both sides of the coin or medal are embossed at once, a ring or collar being adjusted round the medal so as to prevent its swelling out sideways under the pressure.

A large variety of tablet stamping machines are in use. Some are worked by hand, the upper die and collar being attached to a rod or plunger worked by a lever provided with a balance weight, so that by forcibly pulling down the lever the die descends and stamps the tablet. Fig. 166 represents a machine of this description, and figs. 167 and 168 a steam stamping machine, where the impact of the die is given by letting steam into the cylinder by means of the valve handle, so that the piston suddenly rises, and consequently depresses the plunger to which the die is attached on the opposite side of the axis of motion. In another form of machine the necessary impact is given by raising the upper die to which a considerable weight is attached, and then letting it fall, pile-driver fashion.

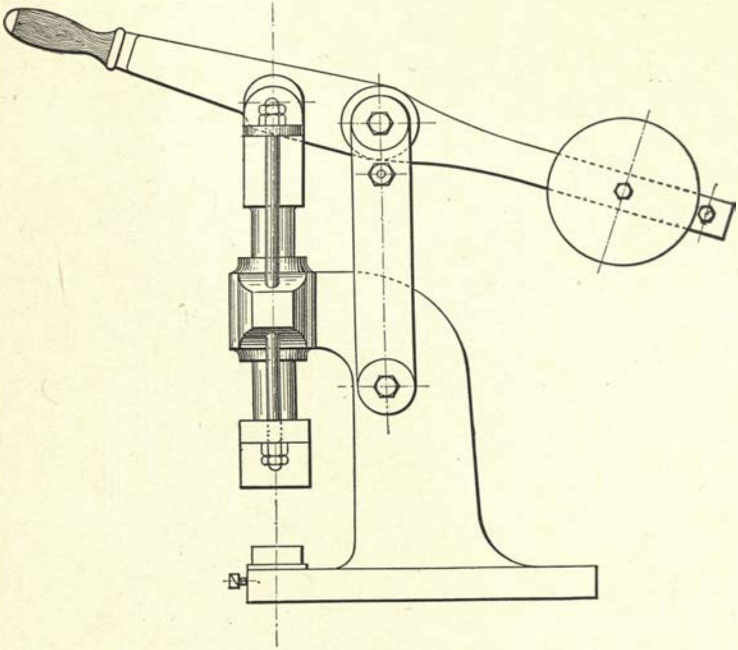
Fig. 166.—Hand Tablet Stamping Machine.

In the case of transparent toilet soaps made by the spirit process (Chap. XXI.), the pan in which the solution of the soap in spirit is effected is connected with a still head and worm, so that the alcoholic vapours evolved are condensed and recovered. With soaps of this class, the liquid soap left when most of the spirit is distilled off is run into frames, so as to gelatinise and solidify, and is then cut up into tablet blanks, which are exposed to the air for a considerable length of time (several weeks or even months) in a warm room, so as to consolidate them by gradual evaporation of remaining alcohol, etc., otherwise they would be too soft to keep their shape properly. Moreover, when freshly prepared the mass is often " muddy " ; but on keeping, it gradually becomes transparent and clear.

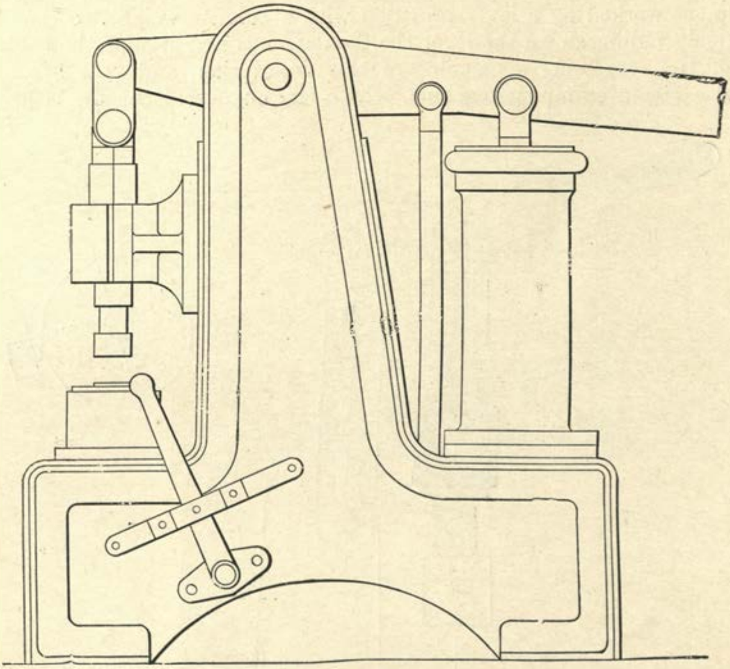

Fig. 167.

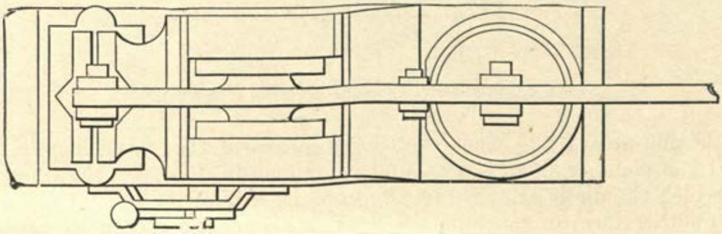

Fig. 168.

Figs. 167 and 168.—Steam Stamping Machine.

Milled Soaps.—Much more elaborate machinery is required for the manufacture of "milled" soaps. The bars of stock soap are first "stripped"—*i.e.*, cut into slices or chips by a slicing machine, actuated like a rotary plane or vegetable cutter. Fig. 169 represents Rutschmann's stripping machine. The chips are dried in a warm air chamber until only a small percentage of moisture is retained, and are then ground between successive pairs of heavy horizontal rollers, so arranged that the soap first passes between No. 1 and No. 2 rollers, then between No. 2 and No. 3, and so on, somewhat as in the case of seed crushing for oil extraction (*q.v.*). Each roller is made to revolve somewhat faster than the previous one, so that the soap slices are not merely *crushed* in passing through, but are also *rubbed;* the soap always adheres to the more quickly moving roller, so that it passes onwards automatically. By means of "doctors" or scrapers, it is detached from the last roller in strips or ribbons, which are returned to the front of the machine and passed through again and again. Fig. 170 represents a form of mill for the purpose.

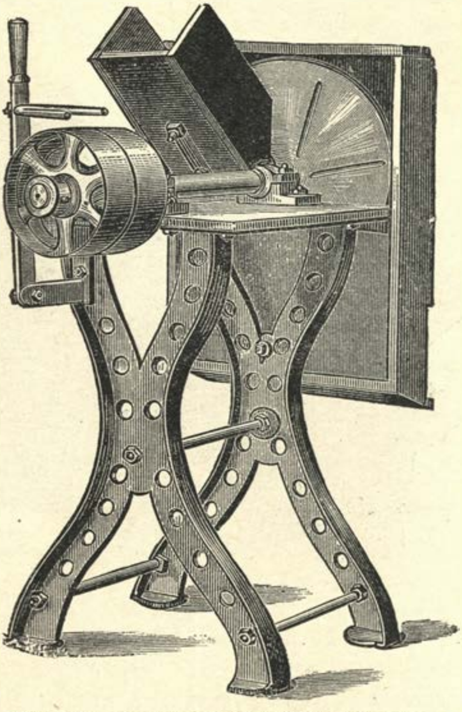

Fig. 169.—Rutschmann's Stripping Machine.

In order to facilitate the preliminary drying of the stock soap, *A. & E. des Cressonnières* (Eng. Pat. 2,446, of 1890) use a series of rollers arranged vertically one above another in an enclosed space heated by steam or hot air, etc. Soap in a just fluid state from the re-melter, etc., passes in a flat stream from a hopper on to the top roller, the contact with which partly solidifies it. The resulting semi-solid sheet passes alternately from right to left, and *vice versâ*, between each successive pair of rollers, as in the mill itself, finally emerging at the bottom in the form of a solid sheet, which is separated by an automatic cutter into strips. The temperature of the chamber and the rate of soap supply are so adjusted that the strips are sufficiently dried by the time they emerge.

When the various stock soaps used, colouring matters, perfumes, unguents (lanoline, vaseline, spermaceti, etc., as required in special cases), or medicinal agents, are thoroughly incorporated together in the mill, the whole mass (if not over-dried) becomes comparatively soft and plastic, much as partially dried putty is softened by rolling and working it in the hand. When thoroughly intermixed, the ribbons stripped off the last roller are strongly compressed together. In one class of machine this is effected by introducing them into a barrel or cylinder provided with a conical end terminating in a nozzle, and forcing the mass outwards by means of a piston worked by a screw or by hydraulic power. The plastic ribbons are thus "squirted" outwards through the nozzle as a continuous bar, which is then cut into short lengths and stamped into tablets. In another class of

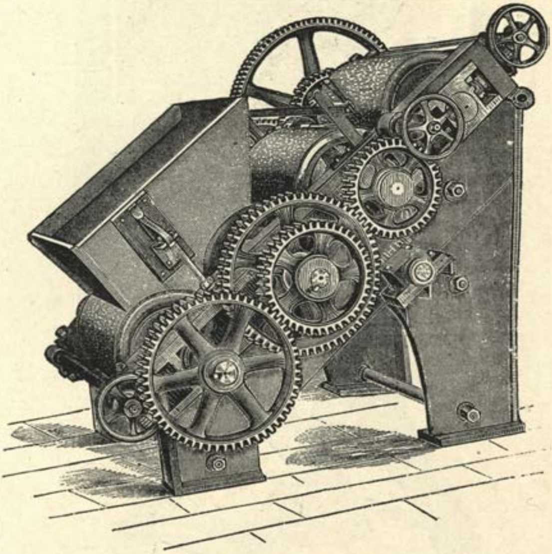

Fig. 170.—Soap Mill.

"plotting machine,"[1] the ribbons are made to fall from a hopper into the grooves of a large conical archimedean screw working in a funnel-shaped barrel, terminating in a nozzle of appropriate size. As the screw revolves the soap is gradually propelled onwards towards the nozzle, and on account of the diminishing diameter of the worm, becomes strongly compressed together, so as finally to issue from the nozzle as a firm solid bar, which is then cut up and stamped as before. Fig. 171 represents Beyer's plotting machine working on this principle.

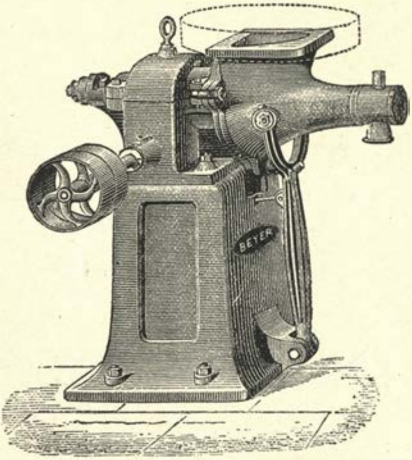

Fig. 171.—Beyer's Plotting Machine.

Cylindrical and spherical soap tablets and wash balls are sometimes prepared. These are usually stamped into approximately the required shape by means of suitable presses, or by hand, and when sufficiently dry, finished by turning and polishing in a kind of lathe.

In order to give a polished surface to soap tablets, a method frequently employed is to expose them to wet steam for a few seconds, so as to glaze the exterior. More expensive varieties are sometimes polished by hand, by means of a cloth dipped in alcohol, etc.

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[1] From the French term, *pelotage*, applied to this squirting process.

CHAPTER XXI.

MANUFACTURE OF SOAP.

As compared with metallurgical and textile industries the art of soap-making is not possessed of any claims to great antiquity. The ancients were acquainted with the detergent power of wood ashes (vegetable alkali) and probably also with that of mineral soda or *natron*,[1] but do not appear to have known anything of the products of the action of these substances on oleaginous materials, no mention of any such compounds being found in Homer or other early Grecian authors; whilst the Hebrew term *borith*[2] used by the prophets Jeremiah and Malachi, although translated "soap," appears to have simply meant *woodash alkali*.

Pliny the elder, however, in the first century A.D. described a sort of imperfect soft soap made from goat's tallow and the alkali from beechwood ash; and also a harder variety (possibly obtained by the action of salt on the former, producing soda soap); and another writer in the second century in a work entitled *De Simplicitus Medicaminibus*, refers to a softer "German" variety of soap (probably chiefly made from the ashes of land plants) and a harder "Gallic" form (probably derived from seaweed ash). Later still, soap-making appears to have been somewhat more extensively practised, as the remains of a soap factory have been found at Pompeii.

Soap-making Processes.—The variations in the different methods by which soaps are prepared on the manufacturing scale are somewhat numerous, but all may be conveniently classified under one or other of the three following heads, so far as the essential parts of the soap-producing processes are concerned. In many cases, however, various subsequent operations are gone through before the goods are finally ready for the market, consisting either of mechanical cutting and shaping operations, such as casting into blocks, cutting these up into slabs, bars, and tablets, and stamping the latter into shape in appropriate presses; or of the addition of other substances to the soap before cooling or solidifying, so as to increase its detergent properties; or to give it special qualities (*e.g.*, disinfecting action); or to harden it,

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[1] Proverbs xxv. 20.—"As vinegar upon nitre (*or soda*, marginal note of Revised Version), so is he that singeth songs to an heavy heart." The frothy non-permanent effervescence due to the action of the acid on *natron* is doubtless what is here alluded to; acetic acid and *nitre* (potassium nitrate) having no mutual action whatever.

[2] Jeremiah ii. 22.—"Wash thee with lye, and take thee much soap." Malachi iii. 2.—"Like a refiner's fire and like fuller's soap."

so as to enable more water or other weight-giving "filling" to be added without rendering it too soft for ordinary scouring purposes, etc.

I. Direct Neutralisation Processes.—In these, free fatty acids and alkalis are brought together and converted into soaps by directly neutralising one another, with or without evolution of carbonic acid gas, according as carbonated or caustic alkalis are employed. Obviously no glycerol is produced in the formation of soaps of this kind.

The free fatty acids thus employed are practically almost confined to the "red oils" of the candle-maker (p. 721)—*i.e.*, the liquid fatty acids expressed from the mixed products of saponification leaving behind the solid acids (commercial "stearine"). Certain distilled and recovered greases (such as Yorkshire grease from the suds of wool scouring, etc., Chap. XII.) are of similar character, and are sometimes intermixed with red oils for the purpose of soap-making in this way; but, as a rule, they are not suitable alone for the preparation of soap of good quality. Resinate of sodium (rosin dissolved in soda lye) used in the manufacture of rosin soaps (*infra*) is a product of precisely similar nature, excepting that the rosin acids do not belong to the ordinary fatty acid families described in Chap. III.

II. Soap-making Processes where Glycerol is set free but not separated from the resulting Soap.—In these processes natural glycerides are employed, being acted on by alkalis (usually caustic) used in regulated quantity so as to suffice to saponify the total fatty matters without introducing any large excess of alkali; the strength of the lye being made such that the product becomes more or less solid after cooling and standing, the glycerol consequently being contained in the product.

To this class belong more particularly *soft soaps* made by boiling together appropriate oils, etc., and potash; *marine soaps* and *hydrated soaps* prepared in similar fashion, usually with soda and largely from coconut or palm-nut oil; so-called *cold process* soaps of various kinds, more especially certain forms of transparent soaps, perfumer's soaps, and analogous products; and certain kinds of soap prepared under pressure.

III. Soap-making Processes where the Glycerol set free and the resulting Soap are separated from one another.—In these processes the essential feature is that glycerides are more or less completely saponified by boiling up with comparatively weak alkaline lyes, and the soap formed "salted out" by the addition of brine or solid salt so as to separate it as a pasty mass from the aqueous fluid in which the glycerol remains dissolved. The half-made soap thus obtained is then finished by one or other of various processes, leading to the production of some variety of "curd," "mottled," or "fitted soap"; whilst the aqueous liquors are either thrown away or boiled down so as to recover more or less of the dissolved salt for use over again, and ultimately obtain the glycerol in an impure form (*vide* Chap. XXIII.). As regards the magnitude of the scale on which they are made, and the total quantity manufactured, boiled soaps of this class are the most important of all.

Additional materials are frequently added to the soap thus prepared for special purposes—*e.g.*, sodium silicate, borax, and sodium aluminate, to increase the detergent action of household and laundry scouring soaps; sodium sulphate and sodium carbonate to stiffen and harden the soap, and prevent it from wasting too rapidly in use; sodium resinate, in the manufacture of yellow soaps; carbolic acid, creosote oils, and similar substances, in the manufacture of disinfecting soaps; and so on.

When potassium carbonate is thus added to melted soda soap in not too large a quantity double decomposition takes place between the sodium salts of the fatty acids and the potassium carbonate, as, for example, in the case of stearate—

$$\overset{\text{Sodium Stearate.}}{2Na\ C_{18}H_{35}O_2} + \overset{\text{Potassium Carbonate.}}{K_2CO_3} = \overset{\text{Potassium Stearate.}}{2K \cdot C_{18}H_{35}O_2} + \overset{\text{Sodium. Carbonate.}}{Na_2CO_3}$$

The result of this is accordingly the formation of a certain proportion of comparatively soft potash soap instead of the harder soda soap, which alters the texture of the mass. This operation of "pearlashing" is consequently employed in the preparation of certain kinds of toilet soaps (*infra*). On the other hand, if fatty matters be saponified with boiling potash lye, and the resulting soap salted out with ordinary salt, the opposite kind of change takes place, soda soap and potassium chloride being formed—*e.g.*, in the case of palmitate—

$$\overset{\text{Potassium Palmitate.}}{K \cdot C_{16}H_{31}O_2} + \overset{\text{Sodium Chloride.}}{NaCl} = \overset{\text{Potassium Chloride.}}{KCl} + \overset{\text{Sodium Palmitate.}}{Na \cdot C_{16}H_{31}O_2}$$

In the earlier days of soap-making, when wood-ash was the most available form of alkali, this reaction was of some technical importance as enabling a hard soda soap to be obtained in lieu of a soft greasy product; but although the effect appears to have been known and the operation practised to some considerable extent, it is doubtful if the chemical nature of the change was understood until recently (*vide* Chap. XXII.).

DIRECT NEUTRALISATION PROCESSES.

The preparation of soap by the direct combination of free fatty acids and alkalis is an extremely simple operation, more especially when the alkali is caustic. All that is required is a suitable mixing pan provided with an agitator so that the fluid ingredients can be intimately intermixed.

Fig. 172 represents a steam-jacketed pan with pipes, *p p p*, projecting upwards into the pan, whilst an agitator, *e*, worked by bevel wheels, carries a series of vertical vanes projecting downwards, so that clots are broken up by the interlacing of the pipes and vanes. Another form of agitator consists of two sets of rods or vanes made to revolve in opposite directions by means of bevel wheels. The red oils, etc., are run into the pan (steam-jacketed for large operations) and heated up; the alkaline lye is gradually run in with agitation; and finally the hot pasty mass is transferred to a "frame" in which it solidifies to a block of soap.

A slight surplus of alkali is practically imperative in order to ensure complete conversion of the fatty acid into soap. This surplus remains for the most part disseminated through the mass as it solidifies, although a small quantity generally exudes as a watery fluid. By carefully regulating the quantities used, the excess may, when required, be diminished considerably below that indicated in the example given below, where 5 parts of free alkali are reckoned for 40 combined, representing a ratio of 1 to 8 or 12·5 to 100. On the other hand, for soaps intended to be highly detergent a larger excess of alkali is intentionally used.

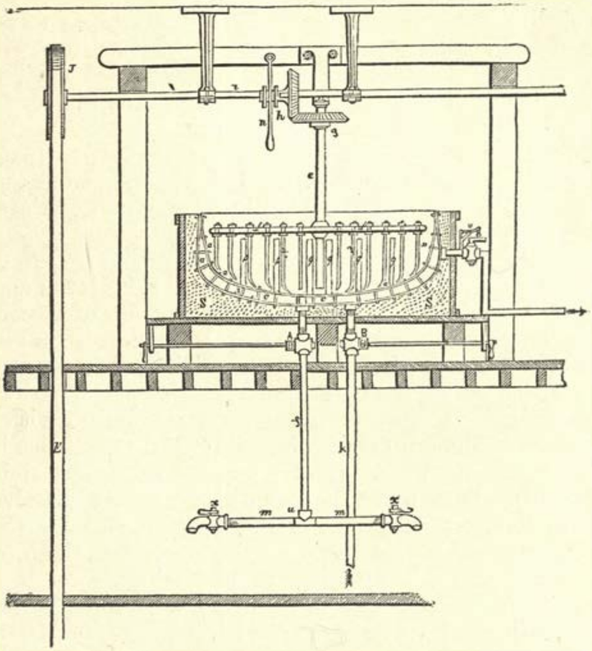

Fig. 172.—Steam Jacketed Pan and Agitator.

Carbonated alkali is sometimes used, instead of caustic, in the preparation of "oleine soap" (Morfit's process). Of late years, however, the facilities for obtaining solid caustic soda as a commercial product have increased so largely that the slight saving in cost effected by the use of the former is generally considered to be more than outweighed by the increased amount of trouble involved in the process.

When carbonated alkali is employed, the mixing pan is fitted with a large movable "curb" (a funnel or barrel-shaped top—fig. 146) to receive the froth produced by the liberation of carbon dioxide, and the operation is carried out somewhat more slowly to prevent the liquid from frothing over.

In the case of inferior soaps, largely made from recovered greases and such-like materials, sodium silicate is sometimes mixed or "crutched" into the mass when the combination is complete, just before running into the frames. For this purpose crutching machines, such as those represented by figs. 160 to 163, are conveniently used. Sodium resinate is also employed as an ingredient to increase the detergent action. On the other hand, with soaps required to contain as little free alkali as possible, not only is great care taken to reduce the proportion of free alkali present to the minimum consistent with proper combination of the fatty acids, but in special cases—*e.g.*, for wool-scouring soaps and soaps used in the silk industries, further means are adopted to render the small excess innocuous.

One method, found in practice to be very effective (patented by the author, A.W.), consists in the addition of a regulated quantity of an ammoniacal salt (usually dissolved in a minimum of water) to the pasty mass, and thorough incorporation of the mixture by a crutching machine or otherwise before running the soap into the frame. Any free alkali is thus neutralised by the acid contained in the ammoniacal salt, with the formation of an equivalent amount of free ammonia. Most of the latter escapes when the soap is cut into bars and stored, but the little that remains, unlike the original free fixed alkali, is beneficial rather than injurious to wool and silk.

Sodium resinate is often prepared for intermixture with soaps of various kinds by boiling up resin with rather less than twice its weight of soda lye of about 16° T. (specific gravity 1·08), containing about 7 per cent. of sodium hydroxide[1] until completely dissolved. The liquid, on cooling, sets to a sort of thin jelly, containing the sodium salts of the resin acids and more or less excess of alkali, according to the quantity used. Any kind of pan will answer if furnished with a wet steam coil, or with an agitator and some other suitable means of heating. Morfit's steam twirl (fig. 144, p. 789) answers well.

Calculation of Quantity and Strength of Lye required, and of Composition of resulting Soap.—The quantity of lye of a given strength employed depends partly on the mean equivalent of the oleine, etc., used, and partly on the amount of excess of alkali intended to be added to ensure complete neutralisation and communicate extra detergent properties to the soap; whilst the exact strength employed depends on the proportion of water the finished soap is intended to contain. Assuming the oleine to be pure oleic acid, its saponification

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[1] The saponification equivalent of resin usually lies between 330 and 370, so that 100 parts of resin correspond with 10·8 to 12·1 parts of NaOH.

equivalent would be 282—*i.e.*, 282 parts of oleine would neutralise 40 of NaOH in accordance with the reaction

Oleic Acid.		Sodium Hydroxide.		Sodium Oleate.		Water.
$C_{18}H_{34}O_2$	+	NaOH	=	$NaC_{18}H_{33}O_2$	+	H_2O

Supposing the lye to be a pure solution of sodium hydroxide, if such a quantity were used as would contain 45 parts of NaOH, 5 would consequently remain unneutralised, or the "free alkali" would bear to the "combined alkali" the ratio of 5 to 40 = 1 to 8 = 12·5 per cent. If, then, 140 parts of lye were used, containing 45 of NaOH (32·1 per cent.), neglecting mechanical losses and evaporation, the resulting mass would consist of 282 + 140 = 422 parts, made up thus—

Sodium oleate, ...	304 parts	=	72·04 per cent.
Excess of sodium hydroxide, . .	5 „	=	1·18 „
Water, ...	113 „	=	26·70 „
	422		100·00

The 113 parts of water are made up of 140 − 45 = 95 parts contained in the lye used, and 18 parts formed by the above reaction.

If a proportionately larger amount of weaker lye were used, containing 45 parts of NaOH in 160 (28·1 per cent. of NaOH), the resulting mass would consist of 282 + 160 = 442 parts, made up thus—

Sodium oleate, ...	304 parts	=	68·78 per cent.
Excess of sodium hydroxide, . .	5 „	=	1·13 „
Water, ...	133 „	=	30·09 „
	442		100·00

On the other hand, if a proportionately smaller amount of stronger lye were used, containing 45 parts of NaOH in 120 (37·5 per cent. of NaOH), the composition of the resulting 282 + 120 = 402 parts would be—

Sodium oleate, ...	304 parts	=	75·62 per cent.
Excess of alkali, ...	5 „	=	1·24 „
Water, ...	93 „	=	23·14 „
	402		100·00

In similar fashion the strength and quantity of lye necessary for any other given mixtures of free fatty acids can be calculated. Thus suppose the mean equivalent of the fatty acids to be E, and that the surplus free alkali is to be n per cent. of that combined as soap; then for E parts of fatty acid a quantity of lye must be used containing $40 \times \frac{100 + n}{100} = 0{\cdot}4 \times (100 + n)$ parts of NaOH altogether. With a lye containing saline matters (chloride, sulphate, etc.) representing m parts per 100 of NaOH, the quantity of saline matter will be

$\frac{m}{100} \times 0{\cdot}4 \times (100 + n) = 0{\cdot}004 \times m \times (100 + n)$; so that a weight, W, of lye will contain—

NaOH,	$0{\cdot}4 \times (100 + n)$
Saline matters,	$m \times 0{\cdot}004 \times (100 + n)$
Water,	$W - 0{\cdot}004 \times (100 + m)(100 + n)$

Hence the total water present will be—

$$18 + W - 0{\cdot}004 \times (100 + m)(100 + n),$$

and the resulting soap will consist of—

Sodium oleate,	$E + 40 - 18$	$= E + 22$
Excess of NaOH,	$\frac{n}{100} \times 40$	$= 0{\cdot}4 \times n$
Saline matters,	$\frac{m}{100} \times 0{\cdot}4 \times (100 + n)$	$= 0{\cdot}004 \times m \times (100+n)$
Water,		$W + 18 - 0{\cdot}004\,(100 + m)(100+n)$
Total,		$E + W.$

Suppose that w parts of sodium resinate solution be added to the soap, consisting of—

Sodium resinate,	a parts.
Excess of NaOH,	b ,,
Water,	$w - (a + b)$,,

then the total mass, neglecting mechanical loss and evaporation, will consist of—

Soap (sodium oleate + resinate),	$E + a + 22$
Excess of NaOH,	$0{\cdot}4 \times n + b$
Saline matters,	$0{\cdot}004 \times m \times (100 + n)$
Water,	$W + w' + 18 - \{0{\cdot}004\,(100 + m)(100 + n) + a + b)$
Total,	$E + W + w.$

If, on the other hand, w' parts of sodium silicate be added, containing—

Sodium silicate and other saline matters,	c parts.
Excess of NaOH,	d ,,
Water,	$w' - (c + d)$,,

then the total mass will contain—

Sodium oleate,	$E + 22$
Excess of NaOH,	$0{\cdot}4 \times n + d$
Sodium silicate and other saline matters,	$0{\cdot}004 \times m\,(100 + n) + c$
Water,	$W + w' + 18 - \{0{\cdot}004\,(100 - m)(100 - n) + c + d\}$
Total,	$E + W + w'.$

These various quantities are readily calculated into percentages when the values of E, m, n, a, b, c, d, W, w, w' are given for any particular case—*e.g.*, suppose $E = 280$, $n = 10$, $m = 12$, and $W = 150$ in the case of a soap not treated with resinate or silicate, etc., then the composition is—

Sodium oleate, . . .	$280 + 22$	$= 302{\cdot}0$	$= 70{\cdot}23$	per cent.
Excess of NaOH, . . .	$0{\cdot}4 \times 10$	$= 4{\cdot}0$	$= 0{\cdot}93$	,,
Saline matters, .	$0{\cdot}004 \times 12 \times 110$	$= 5{\cdot}28$	$= 1{\cdot}23$	,,
Water, .	$150 + 18 - 0{\cdot}004 \times 112 \times 110$	$= 118{\cdot}72$	$= 27{\cdot}61$	,,
Total, . . .	$280 + 150$	$= 430{\cdot}00$	$= 100{\cdot}00$	,,

and similarly in other cases.

SOAP-MAKING PROCESSES WHERE THE GLYCEROL IS SET FREE BUT NOT SEPARATED.[1]

The methods of this character may be divided into three classes according to the temperature and pressure employed. In so-called "cold process" soaps the materials to be saponified and the alkaline lye are intimately intermixed in open vessels at temperatures usually considerably below the boiling point, and allowed to stand until the action is complete, the lyes used being of sufficient strength to yield a product not too moist.

"Hydrated" soaps (including "marine" soap) and "soft" soaps are prepared by boiling together the materials under the ordinary pressure; whilst soaps prepared under increased pressure are treated in closed vessels so as to obtain a still higher temperature for the purpose of shortening the operations and rendering them more complete.

In all cases the amount of alkali employed must be carefully proportioned to the quantity of fatty matters used and their mean saponification equivalent, otherwise either an imperfect soap will result containing more or less unaltered grease owing to the use of a deficiency of alkali, or a strongly alkaline one through the use of too great an excess. Sometimes these two faults occur simultaneously through the action not having been completely carried through. This is not infrequently the case with soaps made on the small scale from highly scented materials (perfumer's soap), where it is essential to avoid too great a rise of temperature, since otherwise the delicacy of the odour would be deteriorated; so that the product is apt to contain simultaneously unaltered fatty glycerides and uncombined caustic alkali.

Soaps of this kind, however, have now been largely driven out of the market by "milled" toilet soaps, in which the evil effect of heat on delicate perfumes is avoided, and at the same time a perfectly made soap ensured, by mixing a good kind of stock soap with the

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[1] During the war the demand for glycerol for the manufacture of munitions made it necessary to separate it as completely as possible from the saponified fats. But this alteration is probably only temporary.

scenting materials, etc., by machinery, grinding them together in the cold (*vide infra*, also p. 808).

Cold Process Soaps.—For the preparation of cold process soaps on the large scale a "Hawes' boiler" is convenient. The fatty matters (tallow, either alone or mixed with palm oil or lard, and preferably a small quantity of coconut oil, the presence of which facilitates the saponification; or other similar mixtures) are introduced into a pan such as that indicated in fig. 173, or into a horizontal cylinder, fig. 174 (5 to 6 feet diameter), provided with a mechanical agitator and heated till sufficiently fluid, usually to about 45° C. (about 113° F.).

Strong soda lye of about specific gravity 1·33 (66° Twaddell, containing about 24 per cent. of $NaOH$) is then run in in sufficient quantity (approximately two parts of fat to one of lye, the exact proportion varying with the mean saponification equivalent of the fatty matters), with continuous agitation until the whole becomes pasty and thoroughly intermixed. The paste is then run out into a wooden frame and well covered up to keep in the heat. As warmth is produced by the saponification change, the mass does not cool until the action is completed. At first the change takes place but slowly, but after a while it becomes more rapid and the temperature perceptibly rises, whilst by and bye, as the action approaches completion, it begins to fall again.

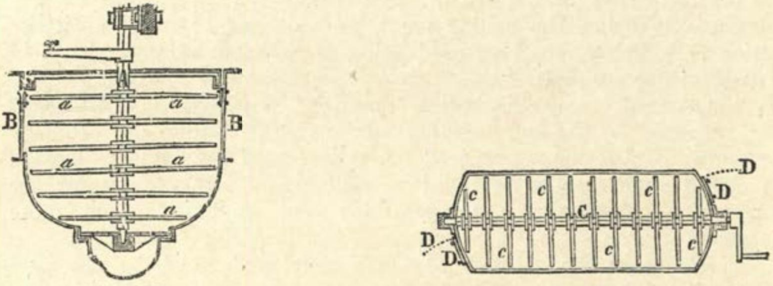

Fig. 173. Fig. 174.

Figs. 173 and 174.—Hawes' Boilers for Cold Process Soaps.

If the materials are too highly heated at first the paste is apt to be too fluid, so that unsaponified grease and aqueous lye tend to separate partially during the period of standing, thus yielding an imperfect product. Instead of soda alone a mixture of soda and potash (the former largely predominating) is often employed with the object of obtaining a product of superior texture.

Transparent Soaps.—Certain kinds of transparent soaps (often termed "glycerin soaps") are frequently prepared by means of a modification of the cold process. The warm fatty materials employed (of which castor oil is generally a considerable ingredient on account of the readiness with which it is saponified and its tendency to form translucent soaps) are intimately intermixed with soda lye (and in certain cases a small proportion of alcohol); soluble colouring matters and essential oils and other scents are then stirred in, and the whole allowed to stand until saponification is complete. With suitably chosen ingredients and proportions the resulting block of soap is more or less transparent, the presence of the glycerol formed on saponification tending to cause the soap to assume a "colloid" or gum-like structure instead of the semi-crystalline opaque condition usually developed in ordinary soaps.

When alcohol is not used as an ingredient in the mass, the transparency is usually only imperfect, but by incorporating extra glycerol instead a highly transparent mass can be readily obtained. Cane sugar effects the same result, and is commonly employed instead of either alcohol or glycerol on account of its cheapness; but the effect on the nature of the resulting product is by no means the same, inasmuch as saccharine substances are apt to produce a very unpleasant irritating effect when applied to highly sensitive skins. This, moreover, is apt to be greatly aggravated by the presence of a more or less considerable excess of alkali in the soap mass, necessarily added to effect complete saponification,[1] inasmuch as muddiness is apt to be produced if any of the fatty glycerides remain unchanged, which is likely to be the case, unless some excess of caustic alkali is present. It accordingly results that many kinds of transparent so-called "glycerin soaps" are of the worst possible quality from the point of view of liability to excoriate and irritate extremely tender skins; although their appearance, when attractively tinted and agreeably scented, render them apparently very desirable articles.

The cheaper kinds of transparent soap of this description are often extensively "filled in" with liquid paraffin and petroleum hydrocarbons which possess the property of blending with the sugary soap mass without seriously interfering with either its consistency or transparency. Taking into account some 20 to 25 per cent. of "loading" thus introduced, together with some 12 to 18 per cent. of sugar, and 20 to 25 per cent. *at least* of water, it often results that the actual soap present does not exceed 33 to 40 per cent. of the mass. On the other hand, a well-made soap where the minimum possible excess of alkali only has been used, where the rate of saponification and tendency to colloidal structure of the product have been intensified by the use of an admixture of spirit in the original materials, together with a little glycerol instead of sugar, and where no loading has been added, not only contains a far larger proportion of useful ingredients of much better quality, but also for that very reason resists the wasting and solvent action of water (especially when hot) much more completely, and is consequently much more economical in use, as well as comparatively free from corrosive action on delicate skins.

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[1] Transparent soaps made by the "spirit process" (*infra*) are generally free from this defect, although as usually sent into the market they contain considerable amounts of cane sugar.

Soft Soaps.—Potash soaps appear to possess, on the whole, a greater tendency to assume the colloid form than soda soaps, in consequence of which, when prepared from suitable fatty matters, they are more inclined to be jelly-like and transparent or translucent, than to form comparatively hard opaque semi-crystalline masses like ordinary soda soaps; moreover, they are generally deliquescent, so that they do not readily dry up.

The precise texture of a given mass, however, largely depends on the temperature, as in cold weather crystalline grains often form, more especially when the fatty matters used contain palmitic or stearic acid. Soap exhibiting this peculiarity (known as "figging") is generally supposed to be of superior quality for that reason, although on what grounds it is difficult to say; the granular appearance is sometimes imitated by mixing in starch, clay, steatite, etc.

Linseed and other drying oils (poppy-seed, hemp-seed, etc.); non-drying and semi-drying vegetable oils (such as rape, cameline, and cotton-seed) and similar animal oils (train, liver, and fish oils); together with the "red oils" of the candle-maker (crude oleic acid), are those most largely employed in the manufacture of soft soaps, a little tallow being added to furnish stearate for "figging," and in many cases indigo in small quantity so as to give a greenish shade (by conjunction with the yellow tinge of the untinted soap); this tint being natural to hemp-seed oil, and, therefore, artificially imitated in other cases. When whale and fish oils are employed an unpleasant smell is apt to be communicated to linen, etc., washed with such soap.

Considerable practice and skill are required in boiling soft soap, although the actual operations are of the simplest character. The "copper" or pan (usually made of iron plates riveted together boiler-fashion—fig. 144) in which the boiling takes place was formerly mounted over a free fire, but is now generally heated by means of two steam coils, one for "dry steam" (*i.e.*, simply a coil through which superheated steam circulates so as to heat up the contents of the pan), the other for "wet steam" (*i.e.*, a coil perforated with holes, so that when steam is let in from the boiler it escapes into the mass through the holes, heating it up and becoming itself condensed, until the temperature is so high that the steam simply blows through). Figs. 147 and 148 illustrate a pan fitted with the two kinds of steam coils. The mixed fatty matters are run into the copper so as to fill it to about one-fifth or one-fourth of its capacity. The whole is then heated up (by free fire when that is used, by means of the dry steam coil if no free fire is employed), and during the heating potash lye (usually of specific grvaity 1·07 to 1·08) is slowly run in. This lye is found by experience to act better if not completely causticised, a portion (some 15 to 25 per cent.) of the alkali being still carbonated.[1]

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[1] When the soft soap is required to be as nearly neutral as possible, carbonated alkali is undesirable as tending to give a product containing a larger amount of "free alkali" than that obtainable by the judicious use of caustic alkali free from carbonate.

The heat should be so applied, and the rate of supply of lye so adjusted, that by the time that a volume of liquor about equal to that of the oil has been run in, the whole mass is beginning to boil. To prevent frothing over a "fan" (fig. 149) is conveniently arranged over the pan.

The boiling is continued with wet or dry steam, usually the former, with further additions of lye from time to time, until the proper consistency and appearance are arrived at as judged by taking out samples and quickly chilling them. As long as an insufficient quantity of lye has been used a visible appearance of unsaponified fat is manifest, giving a peculiar border to the sample; whilst if excess has been added the sample tends to separate more or less into two different portions, one of soap, the other of aqueous liquor. In this case more oil (agitated and emulsified with a little weak liquor to enable it to mix better with the boiling mass) is added, and so on until the sample sets to a clear translucent mass. Finally the wet steam is shut off and the mass boiled either by dry steam or free fire until sufficiently concentrated by evaporation, when the finished soap is put up in barrels, canisters, or drums for sale.

Some makers prefer to use stronger lyes in the first instance (specific gravity 1·120 to 1·150 = 24° to 30° Tw.), whereby less boiling down is required in the final stage. In some cases a mixture of potash and soda lyes is employed, the former, however, always constituting more than half of the total alkali (60 to 75 per cent.). Soft soap containing soda is apt to become muddy in cold weather, and hence is preferably made only in summer.

The exact nature of the mixture of fatty matters employed is generally regarded as a valuable trade secret. The relative proportions of the constituents are often varied somewhat according to the season; in winter the consistency of the product is usually much greater than in summer, so that in the former case, such a mixture is employed as would (for the same atmospheric temperature) give a softer jelly, and *vice versâ*. For household soft soaps, sodium (or potassium) silicate is sometimes mixed in with the finished soap, whilst rosin is often added to the fatty mixture employed as basis. When the soap is intended for silk and wool scouring, however, such admixtures are highly injurious, partly because of the presence of silicated alkali in the soap, which has a very bad effect on the fibre; partly because soaps thus treated usually contain a larger proportion of uncombined potash or soda, or both, than genuine well-made soft soap.

It is generally supposed that because ordinary wool-grease (suint) naturally contains much potassium and but little sodium, therefore soda has a more injurious action on wool fibre than potash. Apart from the somewhat illogical character of this reasoning, however, there does not seem to be any experimental evidence extant to show that this is really the case; on the contrary, experience seems rather to indicate that, provided a soap is sensibly *neutral* (*i.e.*, devoid of alkali uncombined with fatty acids), it is but of little consequence whether it be a potash soap or a soda soap as regards injury to the fibre of wool during use in scouring; on the other hand, a highly alkaline potash soap, otherwise pure, exerts more deleterious action than a comparatively neutral soda soap; although, without doubt an alkaline soda soap, especially if silicated, is extremely objectionable.

Probably the prejudice respecting the superiority of potash over soda soaps for wool scouring is largely due to the inferiority of the soda (silicated) soaps now manufactured in great quantity for household scouring purposes, when compared with potash soft soaps of good quality as regards the amount and nature of the alkaline constituents present other than true soaps—*i.e.*, compounds with fatty acids. For a well-made soda (oleine) soap devoid of silicate or other forms of "free alkali," such as the de-alkalised soap described on p. 814, appears to be in practice quite as well suited for wool-scouring purposes as the best potash soft soap obtainable.

Hydrated Soaps.—The term "hydrated soap" is often applied to soap manufactured in much the same way as soft soap, but made with soda as alkali, and with fatty matters of such nature as to furnish a comparatively hard opaque product rather than a soft jelly-like mass.[1] Coconut or palm-kernel oil is generally an ingredient in the mixture of fatty matters used, its presence facilitating the saponification of other fats less readily attacked by alkalis. When this substance constitutes the bulk or the whole of the mass, the product is known as *marine soap*, as the solubility in brine of the sodium salts formed from coconut oil is sufficient to enable it to form a lather with seawater.

In some cases other substances are added to assist the lathering process, as, for instance, aqueous extracts of certain algæ (Eng. Pat. 9,090, 1900).

Marine Soap.—This is readily prepared by boiling up together with wet steam coconut or palm-kernel oil, and strong soda lye of specific gravity about 1·15 to 1·175 (30° to 50° Tw.), the latter being run in slowly. Saponification proceeds very rapidly when once started, the mass frothing up and requiring a large pan and curb to avoid loss by boiling over. A boiling temperature, in fact, is not absolutely necessary, nor even desirable to begin with, as the heat liberated by the action rapidly raises the temperature—whence the copious frothing.

Owing to the low saponification equivalent of coconut oil (about 210 to 215), a much larger quantity of alkali is required to bring about complete saponification than is the case with most other kinds of fatty matter; 100 parts of coconut oil correspond with about 19 of NaOH, whereas 100 parts of tallow represent only about 14 parts of NaOH (*vide infra*).

A considerable quantity of sodium silicate is generally run into

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[1] In Germany, soap of similar character is often designated *Eschwegerseife*; in America, the term "Swiss soap" is similarly applied. Soaps of this kind are often intermixed with boiled soaps containing no glycerol, so as to form products of mixed character.

the finished mass and well "crutched in" (*i.e.*, intermixed by agitation). The effect of this is greatly to intensify the natural tendency of coconut oil soap to form a tolerably solid mass, even when incorporated with a considerable amount of water; so that silicated marine soap often contains less than 20 per cent. of actual soap (sodium salts of fatty acids) and upwards of 70 per cent. of water. Such a soap, when heated alone, generally separates into two distinct substances—viz., an aqueous solution of silicate, etc., and a pasty mass of actual soap. On account of this tendency to separation, the crutching of the original mass must be prolonged until solidification is tolerably far advanced, in order to ensure a uniform product. As a general rule, the price at which such highly watered soap is sold is not reduced to anything like the extent that would correspond with the amount of water added.

Hydrated soaps made from mixtures containing palm oil, tallow, bone fat, horse grease, etc., are sometimes silicated, but are more frequently hardened by crutching in a strong solution of sodium carbonate (sometimes together with sodium sulphate), whereby not only extra detergent quality is communicated, but also a greater degree of firmness, enabling a larger proportion of water to be present without rendering the soap too soft for sale. The term "hydrated" (or "watered"), indeed, is originally derived from the circumstance that the method of manufacture enables a product to be obtained containing a much larger proportion of water, and a correspondingly less quantity of actual soap, than was formerly practicable with "boiled soaps" of the third class. Even with these, however, it has been found possible to produce an analogous result by somewhat similar devices, more especially by cautiously crutching in saline solutions (sodium silicate, carbonate, etc.) while cooling and solidifying (*vide infra*).

Hydrated Soaps prepared under Pressure.—A large number of patents have been taken out from time to time for various processes and modifications of plant, intended to shorten and simplify the manufacture of hydrated soaps by causing the reaction to occur at a more elevated temperature under increased pressure. Thus *Tilghmann* proposed the use for soap-making of the same plant as used by him for hydrolysing glycerides by water alone (p. 741). The apparatus that has been generally found to answer best is some kind of autoclave where the mutually adjusted quantities of fatty matter and lye are either run in through a manhole or pumped in through a pipe, and then heated up either by means of a free fire or by blowing in high-pressure steam, much as in the manufacture of "stearine" for candle-making (p. 716).

Fig. 175 illustrates Dunn's plant, consisting of a vertical boiler, B, with manhole and safety valve. The fat and lye are pumped in through the safety pipe, A, and the finished mass ejected through the emptying tube and cock, C. Heat is communicated by means of free firing, the temperature attained being determined by means of a longstemmed thermometer, inserted in a tube filled with mercury or paraffin wax. projecting inwards into the boiler.[1]

In *Bennett* and *Gibb's* process a horizontal boiler furnished with an agitator is employed, somewhat similar to that used by Hawes (p. 818). Into this are continuously pumped at one end the fatty matters to be saponified and soda lyes *not causticised* (sodium carbonate solution), containing the appropriate quantity of alkali (30 to 33 parts of soda ash at 48 per cent. Na_2O dissolved in 100 of water to 100 of fatty matter). At the other end the finished soap mass emerges through a weighted exit valve, the pressure being maintained at 220 to 280 lbs. per square inch (about 15 to 20 atmospheres, corresponding with a temperature of 190° to 215° C.). At this higher temperature the carbonated alkali is stated by the inventor to act as efficiently as caustic alkali at lower pressures.

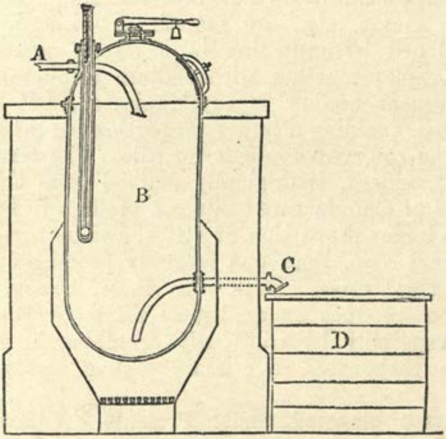

Fig. 175.—Dunn's Plant for making Hydrated Soaps under Pressure.

Calculation of Quantity and Strength of Lye required and of Composition of resulting Soap.—Much the same general principles apply in the case of the soaps at present under discussion as in the case of those prepared by direct neutralisation of fatty acids (p. 814), the chief difference being that in the present instance no water is formed, whilst the glycerol produced instead must be taken into account. If E be the saponification equivalent of a mixture of triglycerides, E parts

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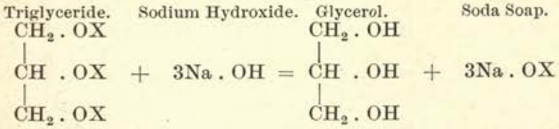
[1] This boiler also serves for the preparation of sodium (or potassium) silicate solution. The boiler is charged with broken up flints or quartz pebbles and soda lye of specific gravity 1·15 to 1·175 (30° to 35° Tw.), and is gradually heated up until a pressure of 4 to 5 atmospheres is attained (corresponding with a temperature of about 150° C.), which is maintained for some hours. At the end of this time the soda has dissolved silica to approximate saturation; the liquor is then blown off into a settling tank, and the clear portion used for intermixture with soap.

by weight of the mixture will require 40 parts of NaOH, or 57·1 parts of KOH, for saponification, and will produce by acting thereon $\frac{92}{3}$ parts of glycerol, in accordance with the equation.


Triglyceride. Sodium Hydroxide. Glycerol. Soda Soap.

$$\begin{matrix} CH_2\,.\,OX & & & & CH_2\,.\,OH & & \\ | & & & & | & & \\ CH\ .\,OX & + & 3Na\,.\,OH & = & CH\ .\,OH & + & 3Na\,.\,OX \\ | & & & & | & & \\ CH_2\,.\,OX & & & & CH_2\,.\,OH & & \end{matrix}$$

Suppose that a soda lye is used, containing m parts of neutral saline matters (chloride, sulphate, etc.) per 100 of NaOH; and that the proportion of lye employed is such that for 100 parts of NaOH converted into soap n parts are employed in excess. The total NaOH employed will, consequently, be $40 \times \frac{100+n}{100} = 0{\cdot}4\ (100+n)$ parts for E parts of fatty matter as before; whilst a given weight of lye, W, will contain, as before—

NaOH,	$0{\cdot}4 \times (100+n)$
Saline matters,	$\frac{m}{100} \times 0{\cdot}4 \times (100+n) = m \times 0{\cdot}004 \times (100+n)$
Water, $W - 0{\cdot}4\,(100+n) - 0{\cdot}004 \times m\,(100+n) =$	$W - 0{\cdot}004\,(100+m)\,(100+n)$
Total,	W

Hence the resulting soap mass (neglecting mechanical losses and evaporation) will contain—

Soda soap,	$E + 40 - \frac{92}{3}$	$= E + 9{\cdot}33$
Glycerol,	$\frac{92}{3}$	$= 30{\cdot}67$
Excess of NaOH,	$\frac{n}{100} \times 40$	$= 0{\cdot}4 \times n$
Saline matter,		$0{\cdot}004 \times m\,(100+n)$
Water,		$W - 0{\cdot}004\,(100+m)\,(100+n)$
Total,		E + W

In the case of a potash soap, if m parts of neutral saline matters be present per 100 of KOH, and if n parts of KOH in excess be used per 100 converted into soap, the total KOH used will be $57{\cdot}1 \times \frac{100+n}{100} = 0{\cdot}571 \times (100+n)$ per E parts of triglyceride mixture; whilst a given weight of lye, W, will contain—

KOH,	$0{\cdot}571 \times (100+n)$
Saline matters, $\frac{m}{100} \times 0{\cdot}571 \times (100+n) =$	$0{\cdot}00571 \times m \times (100+n)$
Water, $\left\{ \begin{matrix} W - 0{\cdot}571\,(100+n) - 0{\cdot}00571 \\ \times\, m \times (100+n) \end{matrix} \right\} =$	$W - 0{\cdot}00571\,(100+m)\,(100+n)$
Total,	W

Whence the entire soap mass produced will consist of—

Potash soap,	$E + 57{\cdot}1 - \frac{92}{3}$	$= E + 26{\cdot}43$
Glycerol,	$\frac{92}{3}$	$= 30{\cdot}67$
Excess of KOH,	$\frac{n}{100} \times 57{\cdot}1$	$= 0{\cdot}00571 \times n$
Saline matters,		$0{\cdot}00571 \times m \times (100 + n)$
Water,		$W - 0{\cdot}00571\,(100 + m)\,(100 + n)$
Total,		$E + W$

Suppose that an admixture of sodium silicate, sodium resinate, syrup, or loading of any kind be made to the extent of w parts by weight, the composition of the total mass will be similarly arrived at. Thus suppose a mixture of fatty matters of mean saponification equivalent 290 ($E = 290$) be saponified with excess of soda lye such that $W = 160$, $n = 15$, and $m = 10$, and that 150 parts of syrup be added per 290 of fatty matters, consisting of—

Sugar,	50 parts.
Water,	100 „
	150

i.e., let $w = 150$; then the composition of the resulting mass will be—

Soap,	$290 + 9{\cdot}33$	$= 299{\cdot}33$	$= 49{\cdot}89$ per cent.
Glycerol,	$\frac{92}{3}$	$= 30{\cdot}67$	$= 5{\cdot}11$ „
Excess of NaOH,	$0{\cdot}4 \times 15$	$= 6{\cdot}00$	$= 1{\cdot}00$ „
Saline matters,	$0{\cdot}004 \times 10 \times 115$	$= 4{\cdot}60$	$= 0{\cdot}77$ „
Sugar,		$50{\cdot}00$	$= 8{\cdot}33$ „
Water,	$160 + 100 - 0{\cdot}004 \times 110 \times 115$	$= 209{\cdot}40$	$= 34{\cdot}90$ „
Total,	$290 + 160 + 150$	$= 600{\cdot}00$	$= 100{\cdot}00$ „

In the preparation of soft soap, the quantity of lye and fatty matter used are usually not adjusted to one another beforehand in the way required for cold process soaps. The lye is run in gradually during the operation until the desired consistency is attained, whilst more fatty matter is added in case of an excess of alkali having been used, practical experience in carrying out the manipulations being the guide to the quantities employed rather than accurate weighing or measuring. Similar remarks apply to most hydrated soaps prepared by boiling in open pans. On the other hand, for soaps made under pressure in autoclaves, etc., the relative quantities of material must be carefully adjusted at the commencement of the operation, as the nature of the process does not conveniently admit of more material being added after the operation has been once commenced and the increased pressure attained.

SOAP-MAKING PROCESSES WHERE THE GLYCEROL AND SOAP FORMED ARE SEPARATED FROM ONE ANOTHER.

Methods of this class substantially depend upon the general principle that whereas most alkali soaps are pretty freely soluble in pure water, especially when hot, the presence of various kinds of neutral saline matter—*e.g.*, common salt—and even of a large excess of caustic or carbonated alkali, renders them insoluble; so that the addition of salt or strong lye to an aqueous soap solution causes the soap to separate or precipitate in more or less solid flakes, the physical structure of which is more akin to that of crystalloid substances than to the colloid gum-like form in which transparent soap is obtained.

The process of manufacture may accordingly be broadly described as consisting of boiling up the fatty matter to be saponified with comparatively weak alkaline fluids not used in excess, but employed in such quantity that when the alkali has been practically all neutralised by combination with the fatty acids the great majority of the fatty matter is decomposed, the remaining portion being distributed through the soap solution formed as a sort of emulsion.

At this stage, on adding solid salt or strong brine, the dissolved soap is thrown out of solution and separates as a more or less granular curd, carrying with it the unaltered fat; the aqueous fluid containing the liberated glycerol being run off, the pasty imperfect soap is boiled up with successive small quantities of stronger lye, the process being continued until the saponification is complete.

Finally, the soap is "finished" by one or other of various kinds of operation, according to the nature of the intended product. For "mottled" soaps, the curd resulting after complete saponification is boiled down (by dry steam, or in the older way of working, by free fire), together with excess of strong lye, until it acquires a sufficient consistency—*i.e.*, until it is so thick that on running into the frames the coloured impurities present (iron soap, etc., formed during the process, or produced by adding green vitriol, etc., to the curd) are unable to sink to the bottom by gravitation; in which case, as the mass cools and solidifies, these coloured matters segregate into veins producing "mottling" of the old-fashioned type.[1]

For "fitted" soaps, the curd produced after complete saponification is effected is allowed to stand awhile so as to separate from the lyes. These are run off, and the curd boiled up with wet steam and weak lyes or water until it is sufficiently thinned in texture to permit of the coloured heavier metallic soaps falling to the bottom by gravitation on standing. With rosin soaps more particularly, peculiar textures ("coarse fit," "fine fit") suitable for different purposes are thus obtained.

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[1] Totally distinct from the modern mottled soaps of highly watered and silicated character—*vide* p. 833.

Curd Soap.—For "cleansed" curd soaps, the diluted curd thus freed from coloured impurities is pumped off into another copper, and there boiled up with dry steam and a small quantity of strong lye until again concentrated to the required extent (*i.e.*, until the curd, freed from lye by subsidence, has the desired proportion of water associated with it); the water retained by the curd being less the longer the boiling is continued, and the stronger the lye (pp. 831, 846).

In boiling for curd soap,[1] the first saponification operation is usually carried out by running into the copper caustic lyes of strength not exceeding specific gravity 1·05 to 1·075 (10° to 15° T.),[2] together with the melted fatty material, and boiling them up together. The way in which this is done varies much in different cases and in different districts. Sometimes the whole batch of "goods" (fatty matters) is run in, and then a fraction of the lye, and the whole boiled up, more lye being added from time to time. Sometimes the greater proportion of the lye is run in first, and the goods added in successive portions, with continuous boiling. More frequently the lye and goods are run in alternately until the full complement of the latter is in the kettle, with somewhat less than the corresponding quantity of lye, the rest of which is subsequently added.

When wet steam is used to heat up the copper the lyes initially employed may be a little stronger than if dry steam be used, on account of the dilution with condensed water. The later lyes may also be stronger than the first ones, as they become greatly diluted with the water already present from the former lyes. The effect of the action of the hot lye on the melted fatty matter is to "kill the goods"—*i.e.*, to emulsify the whole, so that no distinct layer of melted fat rises to the surface on taking a sample.

When the saponification has proceeded to such an extent that a large fraction of the glycerides is acted on and but little alkali remains dissolved in the lye, the whole mass forms a homogeneous pasty mass, consisting of the half-made soap with portions of emulsified fatty

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[1] British curd soaps are almost invariably made from tallow as the chief basis, the characteristics of pure tallow soap (hardness and difficulty of lathering) being modified by the addition of other oils and fats (small quantities of coconut oil, more or less cotton-seed or earth-nut oil, lard, and so on), according to the object in view. On the Continent, and especially in France, vegetable oils are used in much larger proportion. Thus Marseilles (Castile) soap was once supposed to be made almost wholly from olive oil, though earth-nut oil is now commonly used; and even in those cases where tallow is employed, a pretty large proportion of mixed vegetable oil is generally also added, rape oil being usually one of the constituents added to give lathering qualities.

[2] Lyes containing more than some 5 per cent. of Na_2O act much less slowly on tallow and most other oils and fats than weaker solutions, at any rate in the first instance. When, however, the action is once fairly started, somewhat stronger lyes may be run in (in small quantities at a time).

matter not yet saponified distributed throughout it.[1] In this state it is known as " close " soap (in some districts, as being in a " hitch " or " glue "). If too much lye has been added this peculiar texture is not attained, a sample taken out on a trowel exhibiting more or less marked tendency to separate into two fluids, one more watery than the other ; whilst, if the boiling has not been continued long enough, or if the lye be too concentrated, a large surplus of undecomposed fat is visible, giving a greasy texture to the imperfectly made soap that thus separates from the aqueous lye. With proper care, guided by indications only obtainable by practical experience, the required physical condition is attained, most but not quite all of the fatty matter being saponified, whilst practically all the caustic soda in the lyes has been used up, furnishing an aqueous soap solution, or thin jelly, throughout which is disseminated a little emulsified fat.

Graining.—The next stage consists in " graining " or " cutting " the soap by the addition of sufficient saline matter to render the dissolved soap insoluble in the resulting weak brine. For this purpose common salt is used, either solid fresh salt or that regained from previous batches of liquor during the concentration to recover glycerol (p. 876) ; or a strong brine is run in.

The quantity added depends on the proportion of water already present in the copper relatively to the soap, which in turn depends on the strength of the lyes used and the quantity of water condensed from " wet " steam. Moreover, soaps containing much coconut or palm-kernel oil require more salt than others, *cæteris paribus*. When sufficient salt is present in the aqueous liquor, a sample of the contents of the copper taken out on a trowel shows a mass of grains of semi-solid soap, whilst a clear aqueous fluid runs away, which should not be

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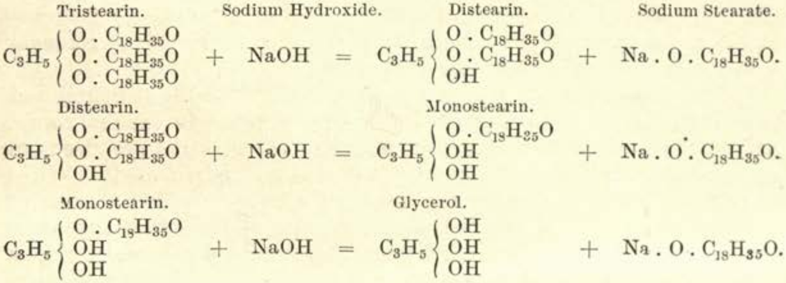
[1] It is extremely probable that the saponifying action of the alkali is exerted in three stages, forming successively one, two, and three molecules of soda soap : thus (in the case of stearin)—



$$\overset{\text{Tristearin.}}{C_3H_5\left\{\begin{matrix}O\,.\,C_{18}H_{35}O\\O\,.\,C_{18}H_{35}O\\O\,.\,C_{18}H_{35}O\end{matrix}\right.} + \overset{\text{Sodium Hydroxide.}}{NaOH} = \overset{\text{Distearin.}}{C_3H_5\left\{\begin{matrix}O\,.\,C_{18}H_{35}O\\O\,.\,C_{18}H_{35}O\\OH\end{matrix}\right.} + \overset{\text{Sodium Stearate.}}{Na\,.\,O\,.\,C_{18}H_{35}O.}$$

$$\overset{\text{Distearin.}}{C_3H_5\left\{\begin{matrix}O\,.\,C_{18}H_{35}O\\O\,.\,C_{18}H_{35}O\\OH\end{matrix}\right.} + NaOH = \overset{\text{Monostearin.}}{C_3H_5\left\{\begin{matrix}O\,.\,C_{18}H_{25}O\\OH\\OH\end{matrix}\right.} + Na\,.\,O\,.\,C_{18}H_{35}O.$$

$$\overset{\text{Monostearin.}}{C_3H_5\left\{\begin{matrix}O\,.\,C_{18}H_{35}O\\OH\\OH\end{matrix}\right.} + NaOH = \overset{\text{Glycerol.}}{C_3H_5\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.} + Na\,.\,O\,.\,C_{18}H_{35}O.$$

According to this view " half-made soap " consists of a mixture of sodium stearate with emulsified tristearin, distearin, and monostearin, uniformly disseminated through the water as a sort of jelly. A circumstance favouring this view is that the quantity of glycerol obtainable from the first spent lyes is considerably less than the amount corresponding with the goods killed, being not much above one-half as a rule.

markedly alkaline to the taste, and should throw up no scum of fatty acids on acidulation; showing that practically all the soda used has been converted into soap, and all the soap formed thrown out of solution by the addition of sufficient salt.

Explosive evolution of steam (violent "bumping") is very apt to occur during the graining process, whence the use of a fan and curb (p. 794) in moderating the frothing, whilst the kettle or copper used is only partly filled with the materials.

After standing for a few hours (steam being shut off) the contents of the copper separate into aqueous "spent lye" which is run off and utilised (for glycerol extraction, etc.), and pasty "grain soap" consisting of about 3 parts of actual soap to 2 of adherent water. This is either finished at once (usually pumped off into a smaller copper, or mixed with another batch from another copper, there being less liability of violent frothing over during the subsequent stages); or else more goods are added with weak lye and the boiling recommenced as before until the new batch of fatty matters is properly "killed," when the whole mass is again salted out.

The grained soap, freed from spent lye, is then boiled up with wet steam, and an additional quantity of somewhat stronger lye containing some 9 per cent. of NaOH (specific gravity about 1·09 to 1·11) gradually run in so as to complete the saponification; the quantity finally added being sufficient to cause the mass to separate into two layers (aqueous lye and soap paste), the excess of sodium hydroxide throwing the soap out of solution just as salt does. In some cases this operation is carried out in two stages, the alkaline "half spent" lye run off in the first stage being utilised for killing fresh goods. This lye washes out entangled brine and contains most of the remaining glycerol liberated by the completion of the saponification. In the second stage sufficient water is added (including that condensed from wet steam) to cause the paste again to assume the "close" state by dilution of the lyes admixed with it, and the boiling continued long enough to ensure the saponification of the last portions of glycerides, when the soap is again grained or "made" by running in sufficient stronger lye to throw it out of solution in grains.

Finally the half-spent lyes are partly, but not wholly, run off, and the soap paste and remaining lye boiled up by means of the dry steam coils, so that water is evaporated, whereby the residual lye becomes more concentrated, and the soap paste less watery (p. 828). When the paste sets on cooling to the required consistency and degree of hardness, the boiling is stopped, and the mass allowed to stand some hours so that the lyes and curd may thoroughly separate from one another, the curd being then transferred to the cooling frames. Unless purposely watered or boiled down to a less extent, curd soaps generally contain only 20 to 25 per cent. of water. When required to be as white as possible, the curd is allowed to stand for some time before the final boiling operation, so that coloured impurities may subside; after which the "cleansed" curd is ladled or pumped off into another copper in which the boiling down with close steam is effected.

The time occupied during these various operations varies with their scale and the skill of the workman. With batches of 40 to 50 tons of goods (tallow and rosin for yellow soap) the "killing" may be effected by an experienced hand in one day, and the further process up to "making" the soap carried out on the next day, the whole being finished on the third day (*Lant Carpenter*).

British curd soaps are usually made with tallow as the chief ingredient, with comparatively small admixtures of other oils and fats. They do not lather very freely, and "waste" in hot water less rapidly than many other kinds of soap. The term "curd" soap, however, does not necessarily denote a tallow soap, but rather a soap boiled in a particular way.

Fitted Soaps.—In the manufacture of curd soaps more or less of the alkaline lye on which the soap is finally boiled, is necessarily left entangled in the interstices of the soap, incompletely removed by gravitation whilst standing; so that on analysis a curd soap thus prepared always shows a considerable proportion of "free alkali." In order to eliminate this an operation termed "fitting" is carried out, more especially in the case of rosin (yellow) soaps, whereby a peculiar texture is attained as the result. The "made" soap is allowed to stand some twelve hours or more so as to bring about as complete separation of lye and curd as possible, and the half-spent lye completely pumped away. Wet steam is then introduced, the condensation of which dilutes the lye still entangled in the interstices of the soap grains.

At a particular stage of dilution (attained if need be by adding more water or a little stronger lye if the dilution has gone too far) the mass of soap acquires the property of allowing an aqueous soap solution to separate at the bottom of the mass on standing (for some days with large batches, for twenty-four hours with smaller ones), whilst the rest of the soap forms a mass of jelly-like flakes, which solidify on cooling to a yellow, somewhat waxy, and translucent solid, usually containing a little under 30 per cent. of water.

Before this cools, it remains sufficiently soft to allow all dirt and solid impurities, such as coloured metallic soaps (containing iron, etc.), to subside by gravity, so that the lowest aqueous layer is very dirty and much discoloured, and in consequence is known as the "negur" (sometimes spelt negre, nigre, nigger, etc.). The uppermost layer of the "neat soap" resting on the negur generally solidifies whilst standing to a solid frothy crust known as the "fob."[1]

The character of the "fit" attained, whether "fine" or "coarse," is judged by the indications observed on sampling the mass from time to time with a trowel. When the physical indications known by

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[1] Society has been compared with a pot of porter, "dregs at foot, scum at top, and good liquor in the middle." A copper of fitted soap with "negur" and "fob" as the extremes and clean "neat soap" in the midst, would be quite as apt a comparison.

experience to denote the desired constitution of the mass are observed, the boiling is stopped, the copper covered over to keep in the heat, and the whole allowed to stand at rest for two to six days according to the size of the batch. Finally the cover is removed, the fob carefully cut away, and the still soft and semi-fluid neat soap pumped into the frames. After cooling, fitted soaps generally contain appreciably more water than curd soaps. From 28 to 33 per cent. is usually present in non-silicated genuine fitted soaps. The fob is generally worked up with the next batch; whilst the negur is either worked up with coarse fats and darker rosin and made into a brown rosin soap, or is utilised for making mottled soap.

Mottled Soaps.—In the earlier half and middle of the last century the majority of soap manufactured was of the curd class, and being made from lyes directly prepared from black ash without purification, generally contained more or less sulphide of iron, or metallic soaps disseminated through it, these being derived from the impure liquors, or in some cases purposely added (in the form of raw or calcined green vitriol = ferrous sulphate, etc.). The curd was boiled down until the proportion of water was reduced to a quantity not exceeding about 20 to 23 per cent., and more frequently lying between 17 and 20 per cent. It was then left to separate, the lyes drawn off, and the greyish or otherwise coloured mass run into the frames, after having been thoroughly intermixed.

During cooling and solidification the colouring matters (chiefly iron soap) segregated from the rest of the mass into veins; so that when the solid soap was cut across a peculiar characteristic marbling or mottling appeared. By exposure to air the iron soap changed its colour from bluish-grey to red in consequence of oxidation, forming what was known in the Marseilles district as the *Manieau Isabelle*. As this effect could not be produced in the case of a curd soap insufficiently boiled down (on account of the thinner texture permitting the heavier metallic soaps, etc., to sink completely to the bottom, like the negur of a fitted soap), the existence of a mottled appearance came to be regarded as a criterion of good quality, so far as absence of an undue excess of water (say not above 20 per cent.) was concerned.

"Castile," "Marseilles," "Olive," and other mottled soaps of this class, although still manufactured to some considerable extent, are, however, but little made at the present day for household use as compared with other varieties of mottled soaps in which the one especial good point characterising the old mottled soaps is wholly absent—viz., that only a limited amount of water is present.

A considerable degree of skill is required for adjusting the proportions of materials used so that a maximum of water can be incorporated without unduly interfering with the veining of the mass. Usually sodium silicate solution is used as stiffening agent, the fatty matters being selected according to the judgment of the maker, and generally containing a considerable proportion of palm-kernel oil or coconut oil, on account of the property of these oils to form soda soaps possessing considerable stiffness even when largely watered (p. 823). After admixture of the silicate the pigments intended to give the mottle are added, and the mass thoroughly crutched until sufficiently stiffened to run into the frames. These are usually made of wood so as to allow the mass to cool as slowly as possible and cause the mottle to " strike " properly into veins. Soaps thus made and " filled " with water and silicate often contain 50 per cent. and upwards of water and not more than 40 to 45 per cent. of actual soap.

Absolutely no good purpose whatever is fulfilled in communicating a mottle of this kind to household scouring soaps; the only effect is that the public is induced to buy a greatly inferior article on the strength of the reputation for quality gained years ago by mottled soaps of the old style. Whatever advantages may be gained by the addition of silicate as a cheap detergent are wholly independent of the mottling.

A method of preparing hard soda soaps without employing caustic soda (sometimes referred to as the " old German process ") was formerly of considerable importance, although at the present day the relative prices of potash and soda are such as to render the process inapplicable, except in backwoods districts where potashes are more readily obtainable than soda ash or caustic soda. The tallow, or other mixture of fats and oils to be saponified, is boiled up with potash lye (made by causticising potashes with lime) much as in the process of soft soap-making, until a syrupy " close " soap is obtained. This is then salted out by the addition of common salt or brine, whereby a curd is obtained mainly consisting of soda soap, the potash soap and sodium chloride reacting on one another by double decomposition (pp. 812, 849). The curd thus obtained is finished by repeating the operations of boiling up with potash lye to complete the saponification, and salting out so as to transform the bulk of the potash soap still present into soda soap. The curd ultimately obtained after a sufficient number of such treatments is finally boiled up with lye until any entangled salt is washed out, whilst the lye becomes sufficiently concentrated for the curd to separate properly.

In all probability, hard soda soaps were first prepared on a comparatively large scale by this kind of process, rather than by saponification with caustic soda direct; although the use of " maritime alkali " (barilla) appears to have been practised in the Marseilles district as long as the soap manufacture has existed there. In inland districts, however, where seaweed ash was practically unattainable, or at any rate costly as compared with vegetable potashes, this " old German " process was the one chiefly employed for making hard soaps until the discovery by *Leblanc* of the method of preparing soda from common salt that bears his name.

SPECIAL VARIETIES OF SOAP.

Rosin Soaps (Yellow Soaps).—In the manufacture of soaps of this description ordinary rosin (colophony) is used as an ingredient, the mixture of alkaline salts of rosin acids and of fatty acids being peculiarly well adapted for certain purposes. In one process (*Meinecke's*) crude turpentine is added to the soap pan, which is fitted with a still-head, so that the spirit of turpentine volatilised with the steam is condensed and utilised.

A much more frequently used method, however, is to separate the spirit and rosin by the ordinary distillation process, and to mix the latter with the fats, etc., to be saponified, so that a mixture of the alkali salts of fatty and resinous acids results; whilst a further improvement (sometimes termed the "French process" for rosin soap) consists in dissolving the rosin in hot alkaline lye separately (p. 814), adding the resulting sodium resinate solution to the finished soap, well crutching the two together; or adding it to the soap in the pan and intermixing by boiling up for a few minutes.

Another process is to boil the rosin and alkali together in a closed boiler under pressure (*Arledter*, Eng. Pat. 2,822, 1899) (p. 795).

Rosin soaps of the better quality are generally "fitted" (p. 831). When made from sound fatty matters and light coloured rosin ("window-glass rosin") they possess a peculiar (not unpleasant) odour, and are known in the South of England as "Primrose" soap.[1] Such soaps usually contain about 30 to 33 per cent. of water and 66 to 69 per cent. of actual soap (including sodium resinate). Coarser rosin soaps made from dark brown rosin, damaged fats, horse-grease, and the like, have generally a more or less marked unpleasant animal odour, partly disguised by the rosin, or by the addition of nitro-benzene (artificial oil of almonds, or *essence de mirbane*) or other cheap scents.

Rosin soaps are generally preferred as stock soaps for transparent soap-making by the spirit process, as the presence of alkali resinates facilitates the acquisition and retention of the colloid structure necessary for transparency. Moreover, a well-fitted rosin soap will practically dissolve completely in spirit, not leaving behind any sodium carbonate or other insoluble matters requiring separation by subsidence or filtration. A similar product can also be prepared by dissolving in spirit an ordinary curd soap (cut into shavings and dried) simultaneously with rosin, whereby the free alkali contained in the stock soap is neutralised, and an alcoholic solution of mixed fatty and resinous soaps directly obtained.

The determination of the relative amount of resinous acids and fatty acids present in a given sample of soap is in many such cases a somewhat important matter. This may be effected by the methods described on p. 861, *et seq.*

Silicated Soaps.—Household soaps, properly so-called, consist of the alkaline (potassium or sodium) salts of certain organic acids, either belonging to the various fatty acid series, being derived from natural

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[1] In some districts in the North of England the term "primrose" is applied to greatly inferior articles, usually largely watered and stiffened with sodium silicate, so that the actual soap present constitutes considerably less than one-half the mass, like the inferior mottled soaps described on p. 833.

oils and fats, or to other series of more feebly marked acids derived from resins, more especially colophony. The older soaps (of the first half of the last century) were essentially of this character; but a considerable proportion of those now manufactured is cheapened by the admixture of various ingredients possessing more or less marked detergent power, the addition of which enables a given weight of so-called soap to be manufactured from a greatly decreased quantity of fatty matters. Of these detergent substances, obviously the most natural constituents are the alkalis themselves, either in the form of hydroxides (caustic alkalis) or as carbonates; in the manufacture of "oil" soaps (oleic acid soaps, p. 813) these constituents are introduced by the simple process of using a larger quantity of alkaline lye than is equivalent to the fatty acids. In other cases, the alkalis are dissolved in water and crutched into the soap before framing. The introduction of sodium silicate solution has various advantages as compared with that of caustic alkalis, proper incorporation being more easy; whilst for such purposes as scouring floors, etc., there is a distinct advantage in the increased detergent power gained by the introduction. For laundry soaps, on the other hand, the utility of silicates is far less manifest; so much so, that various much-advertised laundry soaps of the present day are purposely prepared without that ingredient (sodium carbonate being in some cases used instead): to which circumstances they largely owe what superiority they may possess over other silicated soaps.

One notable advantage gained by the admixture of sodium silicate with soaps made from cheap soft fats, etc., is that the texture of the bar of soap is considerably stiffened and hardened, so that the soap does not waste so rapidly in hot water or when rubbed against the clothing, etc., to be washed, as it otherwise would necessarily do.

Normandy Soaps (Sulphated Soaps).—In order to harden and stiffen a comparatively soft mass various neutral salts may also be employed, more especially sodium sulphate or thiosulphate. The use of these stiffening agents was originally introduced by Dr. Normandy, not for purposes of adulteration or "filling," but in order to enable useful household scouring soaps to be made from materials that otherwise would give a product too soft for economical use in scrubbing, especially with hot water. When sodium sulphate (Glauber's salt) was used, the crystallised salt (not salt cake) was heated so as to fuse in its own water of crystallisation,[1] the liquid being immediately crutched into the hot soap; from one-fifth to one-third of the weight of the soap being thus added. The soaps thus made rapidly become unsightly through efflorescence; so that their use at the present day is not large, other stiffening agents (more especially alkaline carbonates and sodium silicate) being preferred.

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[1] If salt cake is used, it must be dissolved in the right quantity of water and treated with a little soda ash, so as to neutralise the free acid and precipitate the iron that is present.

Aluminated Soaps.—Sodium aluminate has been proposed, and to some extent used, as a substitute for sodium silicate in the preparation of scouring soaps, for which purpose it does not seem to have any special advantages or marked disadvantages.

Borax Soaps.—The addition of borax to laundry soaps is sometimes made, that salt possessing considerable detergent power without injurious action on textile fibres: it is usually supposed, moreover, to have a special blanching action on linen. Some so-called "borax soaps," however, in the market contain only extremely minute amounts of borax, or none at all.

Phosphated Soaps.—In order to diminish the waste of soap with hard water through double decomposition by the lime and magnesia salts present, *E. Grimshaw* (Eng. Pat. 983, 1890) adds an alkaline phosphate to the soap, with the object of forming calcium and magnesium phosphates instead of lime and magnesia soaps insoluble in water.

Paraffin Oil and Petroleum Soaps.—Hydrocarbons of the paraffin series possess the physical property of forming jellies when admixed with soap solutions under suitable circumstances. A small quantity of soap will thus solidify a large quantity of hydrocarbon, a circumstance taken advantage of in manufacturing "solidified petroleum" for fuel. On the other hand, 10 or 20 per cent. of such oil can be crutched into a hot soap paste without materially interfering with its setting on cooling, so that a large amount of "loading" may be thus effected. With certain kinds of transparent soap (made by the cold process, pp. 818, 842) this addition is frequently made.

For laundry purposes the diluting effect of the hydrocarbon oils is more or less compensated by an increased detergent action. Thus greasy linen, etc., soaped with "paraffin soap" can often be cleansed with less rubbing and friction than would otherwise be necessary, because the hydrocarbon tends to dissolve the grease and so to facilitate the detergent action of the soap so far as other dirt is concerned.

Sand, Fuller's Earth, Pipe-clay, Kaolin, and Brick-dust Soaps.—When soap is required for household or other cleansing purposes to be used in conjunction with fuller's earth, powdered brick-dust or pumice-stone, sand, emery, or such-like materials so as to brighten metallic surfaces, cleanse greasy paint (insides of baths, etc.), and so on, it is often found convenient to prepare blocks of mixed mineral powder and soap for sale. These are made by crutching the pulverised pumice-stone, etc., into the hot melted soap in as large a proportion as is consistent with its sticking together in blocks when cold, and are then sold under various proprietary names, chosen according to the fancy of the maker. For general cleansing purposes such mixtures are often very handy; but the price charged, although moderate enough as regards the weight of the block as a whole is generally high with respect to the quantity of soap actually present. Superior kinds of such soaps, sometimes sold as "tooth soaps," are prepared by incorporating with a good kind of remelted toilet soap some 10 to 20 per cent. of finely powdered marble or pumice-stone, cuttle-fish bone, prepared chalk, kieselguhr, etc., etc.

Disinfectant Soaps.—A large variety of soaps are in the market consisting of ordinary soaps of more or less good quality into which have been crutched, before finally cooling and solidifying, fluid or other disinfecting materials, more especially those derived from coal-tar products—*e.g.*, carbolic and cresylic acids, naphthol, naphthalene and creosote oils, etc.; or the artificial camphoraceous products obtained by the oxidation of oil of turpentine (Sanitas oil); or hydrocarbons, such as terebene; or various inorganic germicide materials. Of these different products, a considerable number are highly valuable for the particular purposes for which they are intended, but the value of others is, at the best, only small as antiseptic and disinfectant agents.

To this category also belong a variety of "medicinal" soaps, usually put up in tablet form like "toilet" soaps (p. 838). In these a stock soap of more or less good quality forms the basis, formaldehyde, pepsin, sulphur, iodine, ichthyol, mercurial preparations, or other substances supposed to exert beneficial action in certain cases when thus applied to the skin, being incorporated either by remelting or milling, or in some cases being added to the mass formed by the cold process before it finally solidifies.

Perborate Soaps.—Soaps containing per-salts such as perborate or persulphate form the subject matter of several recent patents. When these are dissolved in water the per-salt is decomposed and hydrogen peroxide formed, and this has an antiseptic action and increases the detergent power of the soap.

Cold-water Soaps.—Various soaps are sold under this name, the alleged advantage of which is usually stated to be that they will lather freely with cold water and therefore do not require clothes, etc., to be boiled. In many cases a more accurate description would be that they dissolve so freely in hot water as to be highly wasteful when used therewith. They generally consist of more or less watered soaps,[1] containing coconut or palm-kernel oil to give consistency, with a liberal intermixture of potassium or sodium carbonate (less frequently of silicate) to harden and give increased detergent action. In practice they are equivalent to a mixture of true soap and soda crystals, and like sand and brick-dust soaps are accordingly very handy in use; but in general the price is high as compared with the actual amount of soap present.

Soap Powders.—The above remark applies *a fortiori* to these substances, which in general consist of ground-up soda crystals (sometimes of ordinary soda ash) mixed with more or less pulverised dry soap.

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[1] Some few "cold-water" soaps do not contain more than 20 to 25 per cent, of water, and are made with only comparatively small additions of potassium or sodium carbonate, the former being preferably used to soften the texture, a result also partly brought about by the use of semi-drying oils as ingredients—*e.g.*, cotton-seed oil.

They are usually highly efficacious as detergents, but somewhat dear as compared with the value of the alkali and the soap which they contain, taken separately from the water of crystallisation and other inert constituents.

Starch Soaps, Oatmeal Soap, etc.—Numerous patents have been taken out for the preparation of products in which *potato flour*, *starch*, and similar materials are intermixed with ordinary soaps. The advantages of such mixtures are difficult to understand. *Oatmeal*, however, well intermixed with some reasonably good quality of stock soap, enjoys some degree of popularity as a "skin-soap." *Bran* and *gluten* have been used for the same purpose; powdered *india-rubber* or *gutta-percha*, as also *dextrin*, *Iceland moss* and other lichen jellies, *sawdust*, *cornflour*, and various analogous substances.

Soaps for Dyeing.—Certain manufacturers have prepared soaps into which are incorporated various aniline dyes and mordants, so that a fabric washed with these is dyed any colour required.

Soaps intended to obviate the use of "blue" after washing linen belong to this class (Eng. Pat. 15,780, 1894). These may contain rosaniline, chrysaniline, Prussian blue, etc.

A soap that is stated to be superior in many respects to turkey-red oil for use in dyeing has been patented by *Stockhausen* (Eng. Pat. 24,868, 1897). It is prepared by boiling sulphonated oils or fats with a large excess of alkali until a gelatinous mass separates out on cooling the liquid.

TOILET AND FANCY SOAPS.

The term "toilet soap" is generally supposed to denote a superfine variety of soap specially prepared with the object not only of effecting cleansing during ablution, but of doing this in the most delicate way with regard to injurious action on the skin, thus serving as a sort of cosmetic. Some of the so-called toilet soaps in the market well fulfil this description; but, unfortunately, many others are largely advertised and sold which are of a far less satisfactory character, either through imperfections of manufacture (more especially presence of excess of alkali), or because of their having an objectionable action on tender skins through admixture of other ingredients (particularly cane sugar).

Some varieties of so-called toilet soaps are simply household soaps of the finer class, more especially curd and yellow soaps made from first-class materials, cut up into tablets, and stamped into shape by one or other of the various kinds of stamping press referred to on p. 805. As a rule, these are scentless, but sometimes a small proportion of cheap essential oil or other perfume (such as citronella, mirbane, etc.) is crutched in before framing.

More frequently stock soaps of good quality are prepared on the large scale from choice, or at least sound, materials, and are then cut up, intermixed or blended, remelted, and again framed, working on a smaller scale. Usually scenting materials are introduced just before transferring the soap to the frames, and in some cases emollient ingredients or unguents—*e.g.*, lanoline, vaseline, beeswax, spermaceti, or various undecomposed glycerides, such as the finest beef marrow, lard, the so-called " beef stearine " separated from the more fluid fats in the manufacture of margarine (p. 396), etc. Of late years " superfatted " soaps of this description (in some cases made by remelting, in others by milling—*vide infra*) have been somewhat largely " boomed," the special advantage derived from their use being supposed to be that an extremely thin greasy film adheres to the skin after use, which more or less prevents the drying and chapping action otherwise produced by ordinary soaps on tender skins. Opinions differ widely as to how far this alleged advantage is really gained or not, some regarding the presence of a few per cents. of glycerides in the soap as actually furnishing a protective film of the kind, rendering the outer layer of the skin soft and supple; whilst others consider that inasmuch as the action of water on perfectly neutral soap always liberates more or less free alkali, which emulsifies grease and enables it to be washed off, whilst any excess of alkali naturally contained in the soap accelerates the action, the notion of an adherent protective grease film is *a priori* improbable; the advantage of such soaps lying rather in their freedom from excess of alkali and other objectionable skin-roughening substances such as sugar. On the whole, the preponderance of opinion rather seems to be in the direction of regarding non-glyceridic unguents (lanoline, spermaceti, etc.) as being more " emollient " when thus admixed with soap than glyceridic materials such as usually found in " superfatted " soaps—*i.e.*, when all other things are equal, especially absence of free alkali; moreover, the presence of unsaponified fatty matters seems sometimes to facilitate discoloration on keeping through the development of a kind of rancidity.

In some cases " pearl-ashing " (pp. 812, 849) is adopted to improve the texture and lathering power. When this is done the pearl-ash liquor (solution of potassium carbonate) is simply crutched in with the other ingredients before framing. Since an equivalent of sodium carbonate is formed for one of potassium carbonate introduced, obviously, a pearl-ashed soap is apt to be strongly alkaline and objectionable for persons suffering from tender skins, or a tendency to acne or eczema.

Milled Soaps.—" Perfumers' soaps," sometimes known as " little pan soaps," were formerly largely made by perfumers by means of the cold process. The fatty matters thus employed were generally of excellent quality, being mainly the oils and fatty cakes used to absorb flower perfume (odorous essential oils) by packing the fat cakes and flower petals together, or by passing air over the flowers and bringing it in contact with oil, etc., to absorb the volatile odorous matter. After the oil or fat was fully charged by numerous repetitions of the process it was treated with alcohol, whereby a flower essence was obtained by dissolving out the essential oils, leaving behind a delicately scented fat, capable of furnishing a deliciously perfumed soap.

Owing, however, to the necessity for avoiding heat as much as possible in the preparation of the soap, it often happened that these soaps contained simultaneously much undecomposed fat and a large amount of free alkali. Accordingly, of late years they have been largely supplanted by "milled" soaps, consisting of stock soaps of good quality "stripped" or reduced to chips and dried until only a few per cents. of moisture are retained, and then ground (together with perfumes, colouring matters, glycerin, or other emollient ingredients, etc., as required) between rollers until reduced to a stiff, putty-like mass, which is then squirted or screwed into bars and so formed into tablets (p. 809).

The advantages of this method are, firstly, that, inasmuch as no artificial heat is applied, delicate flower perfumes, etc., can be readily incorporated with the soap mass, which it would be impossible to use with a remelted soap because the heat would dissipate or destroy the odorous matter; and secondly, that as the resulting tablets usually contain only a small quantity of water, a given weight of soap tablet generally contains a much larger quantity of actual soap than another tablet of the same weight prepared by remelting or by the cold process, whilst, being harder and stiffer, it lasts longer, wasting less rapidly during use. By suitably choosing the stock soaps used, employing only such as have been prepared from first-class oils and fats, etc., and refined or otherwise treated to remove "free" alkaline matters, "fancy" and "toilet" soaps of the finest possible qualities are thus readily obtainable. Frequently the stock soaps are partly made with potash and partly with soda, so as to arrive at a suitable texture through the softer nature of the potash soap, as well as to produce a better lather.

In this connection it is worth noticing that there is some reason for supposing that soap with which an extremely large proportion of flower essences and essential oils is incorporated, may thereby become less suitable for use by persons with tender skins than would be the case with a lessened amount of odorous matter, inasmuch as many essential oils of the kind possess more or less marked rubefacient (skin-reddening) action, analogous in character to the stimulating and blistering action of mustard, oil of turpentine, and similar substances. It is within the author's own personal observation that when the same high-class soap mass is used for preparing two differently priced fancy soaps, only differing in that the more expensive one is impregnated with a much larger proportion of scent than the other, persons possessing exceptionally sensitive skins can sometimes use tablets made from the less highly scented portion with impunity, whilst the employment of tablets made from the more strongly perfumed portion speedily sets up a disagreeable amount of skin irritation.

From the point of view of irritating skin action, however, the presence of sugar appears to be much more objectionable than that of most scenting materials, even in large quantity. Opaque fancy soaps are rarely, if ever, admixed with this adulterant; but very little transparent soap is, or was, in the market that does not contain more or less.

Brown Windsor Soap.—The term "Brown Windsor" has long been applied to a peculiar brown soap highly esteemed for toilet purposes. Originally this substance deserved its reputation; but as in the case of "mottled" soap, the perverted ingenuity of the modern adulterator has completely altered the character of the great majority of toilet tablets sold under that name.

The "Old Brown Windsor" of a generation or two back was simply a form of soap (usually mostly curd) that had been kept in stock for a great length of time, and occasionally remelted; with the result of acquiring a pretty deep brown tint through oxidation of fatty acids, etc., and of becoming practically wholly devoid of free alkali, any excess of alkali originally present being neutralised by the slightly acid oxidation products formed during keeping or "ageing," or while being remelted.

Such a soap, pleasantly scented at the last remelting before making into tablets, and originally made from suitable materials, lathered sufficiently freely to be conveniently used, and had as little deleterious action on sensitive skins as is compatible with the hydrolytic properties of soaps generally. The modern substitutes, however, are frequently nothing but coarse soaps made from discoloured fats, and further browned by coal-tar dyes or admixture of brown ochre. All sorts of scraps (including floor scrapings) incapable of utilisation in any other way are worked in to the mass, which frequently is alkaline to a highly objectionable extent. In short, advantage is taken of the reputation deservedly gained in former years by an excellent article to sell under the same name a decidedly inferior product. Similarly, so-called "White Windsor" soaps are sometimes to be met with, in many cases made from coconut oil, highly alkaline, and wholly different in character from the genuine old-fashioned brown article.

Transparent Soaps.—As already stated, soap can in many cases assume two distinct physical conditions, one a more or less pronounced crystalline form in which the "grains" retain, associated by a sort of physical attraction, a considerable quantity of water, the amount of which varies with circumstances—*e.g.*, a curd soap, when granulated from a dilute liquor with a minimum of salt or alkali, will contain as much as 35 to 40 per cent. of such associated water, which becomes gradually lessened down to 20 to 25 per cent. or less by boiling down with dry steam or free fire so as to concentrate the lyes.

The other is a structureless colloidal state, in which the soap constitutes a mass which under suitable conditions is clear and transparent like a strong jelly. Soft soaps (potash soaps) appear to have a stronger tendency to retain this colloidal state than hard (soda) soaps, so that it is only with comparative difficulty that they become granular. Soda soaps, on the other hand, although granular when separated from solutions by means of salt, readily become colloidal when dissolved in alcohol, so as to form transparent masses when the solvent evaporates. This physical condition is facilitated in many cases by the presence of various other substances, of which glycerol is one of the best known; so that fats saponified by the cold process, even in the absence of alcohol, often yield transparent products owing to the liberation of glycerol.

Castor oil, in particular, readily yields a transparent product in this way. Cane sugar possesses the same property; and being cheaper and easier to work with in some respects, is largely substituted for glycerol, to the great disadvantage of the consumer, excepting in one respect, viz., that while transparent soaps containing large percentages of glycerol are apt to "sweat," by attracting moisture from the air, sugared soaps do not deliquesce so readily.

Resinates mixed with ordinary fatty acid soaps generally form colloidal masses more readily than the latter alone. Accordingly, rosin soaps are preferred as "stock" when granular soaps are to be rendered transparent. This tendency to transparency is often strongly marked even with water-made rosin soaps of good quality ("fitted" soaps), which generally become translucent and sometimes tolerably clear when spontaneously dried in not too thick masses.

Accordingly, two principal methods are in use for the preparation of transparent soaps. In the "spirit" process the stock soap is dissolved in spirit and treated as described (p. 805), rosin being sometimes added to the mass for the double purpose of aiding transparency and neutralising free alkali.[1] The mass left when the bulk of the spirit is distilled off is usually turbid; but on slow drying in a warm storage room (temperature near 35° C. = 95° F.) it becomes clear, especially when a liberal addition of sugar has been made to the mass before finally casting in the frames. Usually the blocks are cut up into tablets, which are shaped by stamping in blank dies, and then slowly dried, the final impression being given by a later stamping. When glycerol is added instead of sugar, the resulting transparent soap is as innocuous, even to the most sensitive skin, as any kind of soap can possibly be; but the same can by no means be said of sugared soaps (which, at all events and prior to the world's shortage of sugar, constituted the large majority of those in the market), persons with unusually tender skins being generally unable to use such compositions long without suffering more or less severely in consequence.

Similar remarks apply to the transparent soaps made by the other process (cold process, p. 818). When sound fatty and oily matters are used, together with alkali not in excess, no sugar being employed, a superior article is produced; but the great bulk of so-called "glycerine" soap made in this way is, or until recently was, alkaline to an extent highly prejudicial to tender skins, besides being largely admixed

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[1] Some transparent soaps thus prepared when dissolved in water and shaken with petroleum spirit, or when dried and extracted with the same solvent in a Soxhlet tube, will yield several per cents. of uncombined colophony to the solvent.

with sugar,[1] whilst in many cases the oils used (chiefly castor oil, together with coconut oil, etc.) are of such quality as to leave an unpleasant odour on the skin, easily perceptible when the scenting material has evaporated; and in addition, large percentages of valueless "loading" (petroleum hydrocarbons, etc.) are added to increase the weight. In short, transparent toilet soaps, like artificially mottled scouring soaps, are articles in the purchase of which caution is pre-eminently desirable. For further details concerning transparent and other toilet soaps and their manufacture *vide* the author's (*A. W.*) "Cantor Lectures on the Manufacture of Toilet Soaps" (*J. Soc. Arts*, 1885).

Soap Leaves.—A very convenient form of soap for travellers is obtained by melting a good quality of stock soap with a little water, perfuming to taste, and passing sheets of tissue paper through the fluid. The paper thus coated with films of soap is dried and cut up into leaves, one of which generally suffices for ordinary washing of the hands, etc., thus avoiding the necessity of having to carry about a wet cake of soap.

Marbled Soaps and Harlequin Soaps.—A peculiar marbled appearance is sometimes given to soap balls, tablets, etc., by remelting a more or less white stock soap, and running it into a small frame. A comb with wide teeth is then dipped into a colouring composition (melted soap with pigments or dissolved colouring matters), withdrawn, and passed through the semi-fluid soap in the frame, so as to streak it according to fancy. The same method is applicable to cold process compositions, before they have completely solidified. By cutting up pieces of variously tinted soaps into fragments, and scattering them through a cold process transparent soap mass on the point of solidifying, a mixture of transparent soap with variously tinted lumps interspersed is ultimately obtained. When cut up and stamped into tablets, these are sometimes sold as "harlequin soaps." Tablets are sometimes ornamented by stamping a device somewhat deeply, and then filling the grooves with melted coloured transparent soap, etc.

One process of producing variegated soaps consists in piercing the bars with needles, then placing them into a closed vessel, creating a partial vacuum and introducing the liquid colour which fills the holes. The soap is finally washed with a spray of water (Eng. Pat. 3,329, 1896).

Fluorescent Soap.—The addition of fluorescein or similar compounds to a transparent soap causes the latter to be permanently fluorescent, the effect being increased by the presence of ammoniacal salts.

Floating Soaps.—By the addition of various ingredients, such as sawdust (Eng. Pat. 12,953, 1896), or by the introduction of a hollow insert, tablets of soap can be made to float upon water. The use of alkaline peroxide, which has been patented for this purpose, is very

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[1] For a typical analysis of a soap of this kind (not loaded with hydrocarbons) *vide* p. 873.

objectionable, if the soap is to be used for toilet purposes. See also p. 839.

Shaving Creams.—Cold process soaps made from refined lard or other superfine fatty matters and potassium hydroxide, not used in excess, are usually the basis of these preparations. To facilitate lathering, a small quantity of the finest coconut oil is often added. The resulting mass is ultimately ground in a marble mortar, etc., with scenting materials (oil of bitter almonds for *almond cream*, and so on), glycerol or other emollient ingredients being added to taste, and sometimes tinting materials—*e.g.*, a few grains of vermilion per lb.—to give a faint flesh colour, etc. A perfumed concentrated alcoholic solution of soap forms a variety sometimes known as "liquid soap."

Neutralised Soaps.—For certain special purposes it is highly important that the soap employed should be as devoid of free alkali as possible. In order to effect this object a variety of methods have been proposed and more or less largely employed, according to circumstances.

In most cases soaps that have been put through the operation of "fitting" (p. 831) are almost absolutely neutral, any entangled alkaline lye present in the curd before fitting having been washed out during the process. If, however, after "cleansing" in this way so as to separate coloured impurities, the soap be again boiled down on a fresh portion of lye, the resulting curd soap is always considerably alkaline through entangled lye. A method used with some degree of success consists in re-melting (p. 803) the soap to be treated with a small proportion of fatty matter, which becomes more or less saponified by the treatment. Inasmuch, however, as the alkali present is generally carbonated, this method rarely gets rid of all the free alkali, excepting in cases where the additional fatty matters used consist largely of free fatty acids like some kinds of highly hydrolysed palm oil.[1] In the manufacture of transparent toilet soaps by the spirit process, any carbonated alkali present is left undissolved and is, consequently, separated by subsidence or straining; whilst if rosin be directly added, the free alkali present is more or less converted into resinate and so eliminated. When, however, resinous or fatty materials are added to a soap mass in the milling process, no action ensues between them and the free alkali; so that "superfatted" soaps thus prepared (without long continued fusion of the glycerides with the soap by remelting) often contain simultaneously excess of alkali and unsaponified glycerides, like imperfectly made cold process soap (p. 818). The author's (*A. W.*) ammonium salt process, referred to on p. 814, on the other hand, acts equally well in the way of removing "free" alkali, whether applied to soap shavings during the milling process, or to fused soap during remelting, or to soap curd, etc., in the crutching pan; any alkali carbonate or hydroxide being converted into a neutral salt with simultaneous evolution of ammonia, most of which escapes.

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[1] According to A. Watts, the superiority of the madder purples for which the firm of Hoyle & Sons were long famous, was due to their practice of re-melting the best soaps procurable with an additional quantity of palm oil.

CHAPTER XXII.

GENERAL CHEMISTRY OF SOAP—SOAP ANALYSIS.

In addition to various points previously discussed in connection with the general chemical and physical properties of oils, etc., a variety of other matters are of some interest relating to the properties of soaps of various kinds.

As already explained, the term " soap " is ordinarily used to denote the alkali (potassium and sodium) salts of the various fatty acids contained as glycerides in oils and fats, and of the rosin acids contained in colophony and allied resinous matters. Numerous corresponding salts of the alkaline earths and heavy metals, however, exist, all of which, strictly speaking, are also soaps—*e.g.*, the lime " rock " obtained in the manufacture of candle stearine (pp. 718, 722), and the " lead plaster " obtained by mixing together olive oil (or other analogous oil) and litharge. As a general rule, these earthy and metallic soaps are insoluble in water, at any rate as compared with alkali soaps ; so that on adding a metallic salt solution to an aqueous solution of alkali soap, double decomposition occurs, and a precipitate is formed of the metallic soap. Thus, for example, the applicability of Clark's soap test for lime and magnesia in water depends on such actions—*e.g.*, in the case of stearates—

$$\overset{\text{Sodium Stearate.}}{2Na . O . C_{18}H_{35}O} + \overset{\text{Calcium Sulphate.}}{CaSO_4} = \overset{\text{Calcium Stearate.}}{Ca\begin{cases} O . C_{18}H_{35}O \\ O . C_{18}H_{35}O \end{cases}} + \overset{\text{Sodium Sulphate.}}{Na_2SO_4}$$

Similarly Gladding's test (p. 862) for rosin acids in soap depends on the precipitation of silver stearate, oleate, etc., insoluble in ether containing a little alcohol when silver nitrate acts on an alcoholic solution of mixed alkali salts ; whereas silver resinate is soluble in that medium.

Alkali soaps often possess in a high degree the peculiar property of gelatin and other colloid bodies—viz., that whilst on heating with hot water they apparently dissolve to an ordinary solution, on cooling this does not allow crystals of material to form through diminished solubility on account of lowered temperature, but instead sets to a more or less firm jelly. This property of " jellifying " is often used as a practical test of the value of soap for certain purposes. A known weight of soap is dissolved in water (conveniently $1\frac{1}{4}$ ounce to a pint = 20 fluid ounces, or 62·5 grammes per litre) and the solution allowed to cool ; the rate at which the fluid gelatinises, and the texture of the resulting jelly being noted. Preferably the soap is dissolved in about half the total quantity of water, boiling, and when all is in solution the rest of the water is added cold.

Although alkali soaps are usually freely soluble in water, especially when hot, yet the presence of certain other substances in solution prevents their dissolving, whilst the addition of these substances to aqueous soap solution causes the precipitation of more or less of the dissolved soap. Thus the process of "salting out" half-made soap in the open pan boiling process (p. 829) depends on the smaller degree of solubility of soap in brine than in pure water. Similarly when curd soap is boiled down on an alkaline lye, the soap is rendered less and less soluble in the aqueous liquor as the concentration proceeds, and at the end of the operation is wholly insoluble therein, even if partially soluble at first when the lye was weaker.

The proportion of salt, relatively to water, required to render a given soap insoluble, obviously varies with the nature of the fatty acids present. Thus while sodium stearate and palmitate are precipitated from solution by comparatively small amounts of salt, coconut and palm-nut oil soaps are sufficiently soluble to remain dissolved in sea-water, which usually contains 3 to 4 per cent. of dissolved solid matters, mostly sodium chloride. In hot brine the solubility of soap is usually greater than in cold. Thus in the course of a variety of experiments on the solubility of soaps in saline solutions *Whitelaw* found [1] that tallow soap was completely soluble to a clear fluid in a boiling solution containing not more than 3·0 per cent. of sodium chloride, the whole setting to a firm jelly on cooling; whilst palm-nut oil soap dissolved clear in a boiling solution containing not more than 13·0 per cent. of sodium chloride, a large portion of the soap being thrown out of solution on cooling.

The curd thrown out of solution by salting retains an amount of associated water incapable of expression mechanically by moderate pressure in a dry cloth, and hence not in quite the same condition as ordinarily mechanically entangled fluid. The amount of this water varies inversely with the concentration of the saline solution. Thus the longer a curd soap is boiled down on the lye so as to concentrate this, the less is the proportion of moisture retained by the soap after separation from the lye and framing so as to solidify. In similar fashion, *Whitelaw* found that an olive oil soap retained the following amounts of water after half an hour's boiling with different brine solutions :—

Salt in Brine.	Water in Curd.
8 per cent.	31·6 per cent.
17 „	25·7 „
27 (saturated).	19·1 „

Hydrolysis of Soap Solutions.—When soaps are dissolved in absolute alcohol, or in spirit containing but little admixture of water, no visible

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[1] *J. Soc. Chem. Ind.*, 1886, v., 90.

decomposition ensues; a neutral soap gives a solution which has no action on suitable indicators—*e.g.*, phenol-phthalein. If, however, water be substituted for spirit, the soap is more or less broken up into sodium hydroxide and an acid soap—*e.g.*, in the case of stearate—

$$\underset{\text{Sodium Stearate.}}{2Na\,.\,O\,.\,C_{18}H_{35}O} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sodium Hydroxide.}}{NaOH} + \underset{\text{Sodium Acid Stearate.}}{\left\{\begin{array}{l} Na\,.\,O\,.\,C_{18}H_{35}O \\ H\;\,.\,O\,.\,C_{18}H_{35}O \end{array}\right.}$$

A pretty way of illustrating this action is to boil a piece of dried soap with alcohol to which a little phenol-phthalein has been added, and filter the solution into a tall jar or large test-tube; the solution should be strong enough to set to a firm jelly on standing. When set, a little distilled water is poured on the top of the jelly. This hydrolyses the soap in the top layer so as to turn it pink by the reaction on the phenol-phthalein of the liberated alkali. On standing, the water gradually dialyses downward through the colloidal soap mass, and the pink colour descends with it.

By adding salt to an aqueous solution of soap so as to salt out the curd completely, filtering off the latter, and examining the filtrate alkalimetrically, the amount of alkali set free under given conditions can be determined; or the same result can be obtained (with more trouble) by collecting the "salted-out" curd, washing it with brine over the vacuum filter, dissolving the curd in absolute alcohol, and titrating the acidity with phenol-phthalein as indicator. A long series of observations thus made led to the following results:—[1]

Fatty Acids.	Mean Molecular Weight.	Hydrolysis brought about by x Molecules of Water.				
		$x=150$	$x=250$	$x=500$	$x=1000$	$x=2000$
Pure stearic acid, . . .	284	0·7	1·0	1·7	2·6	3·55
Nearly pure palmitic acid, .	256	1·45	1·9	2·6	3·15	3·75
Crude lauric acid (coconut oil), .	195	3·75	4·5	5·4	6·45	7·1
Pure oleic acid, . . .	282	1·85	2·6	3·8	5·2	6·65
Crude ricinoleic acid, . .	294	1·55	2·2	3·0	3·8	4·5
Chiefly stearic, palmitic, and oleic acids (palm oil tallow soap), ...	271	1·1	1·55	2·6	4·1	5·3
Chiefly tallow and rosin (primrose), ...	280	1·5	2·2	3·1	4·2	5·3
Cotton-seed, ...	250	2·25	3·0	5·0	7·5	9·5

Fig. 176 represents these results in the form of curves, from which it would seem to result *inter alia* that amongst homologous soaps

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[1] Alder Wright and Thompson, *J. Soc. Chem. Ind.*, 1885, iv., 625; Alder Wright, "Cantor Lectures," Society of Arts (*J. Soc. Arts*, 1885, xxxiii., 1124).

(stearic acid, palmitic acid, coconut oil acids) the higher the molecular weight the less rapid the hydrolysis.

If extra alkali be added to the soap solution, the hydrolytic effect is proportionately weakened, as suggested by the character of these curves, concave downwards. Thus the following figures were obtained with some of these same soaps :—

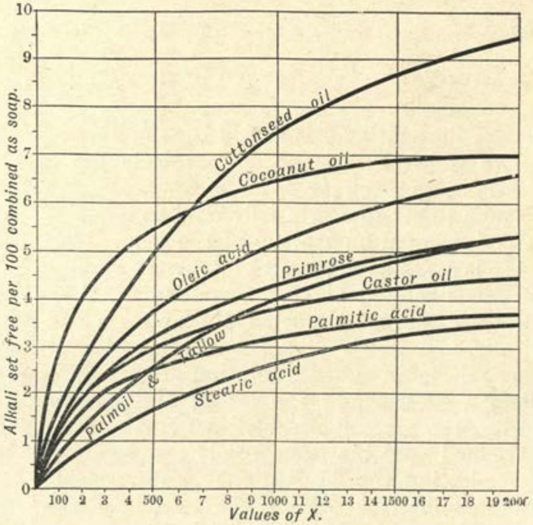

Fig. 176.—Alder Wright's Chart of Hydrolysis of Soap Solutions.

Nature of Fatty Acids Used.	Extra Na_2O added to Solution, per 100 combined as Soap.	Hydrolysis brought about by x Molecules of Water.		
		$x = 50$	$x = 250$	$x = 2000$
Crude lauric acid (coconut), .	11·0	1·1	1·6	2·0
Cotton-seed oil soap, . . .	15·0	nil.	nil	6·5
Stearic and oleic (tallow), . .	20·0	nil.	nil.	nil.
Tallow rosin (primrose), . .	15·0	nil.	0·1	1·3

The property of becoming hydrolysed by water has a great deal to do with the cleansing and detergent action of soap ; the minute amount of alkali set free helps to emulsify greasy matters, and thus greatly facilitates their removal by washing out under friction.[1]

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[1] Pickering (*Chem. Soc. Trans.*, 1917, cxi., 86) has described experiments which show that the detergent action of soap must be attributed partly to its power of emulsifying oil, the globules of which become coated with a pellicle which prevents them from rendering adjacent objects oily : partly to the low surface tension between the soap solution and the oil, and possibly, in part, to the acid soap produced in the hydrolysis forming a colloidal compound with the dirt.

Reactions of Soap Solution or of Melted Soap with Inorganic and other Salts.—When a solution of sodium chloride is added to one of a soda soap, or one of potassium carbonate to a potash soap, there being but one base present, obviously, no tendency can exist towards double decomposition and exchange of bases; but it is otherwise if sodium chloride be added to a potash soap, or potassium chloride to a soda soap; or if potassium carbonate be added to a soda soap or sodium carbonate to a potash soap. In certain of these cases it is well known that double decomposition ensues. Thus, if a potash soap be made by boiling fatty matter and wood ash lye together, and sodium chloride be then used to salt it out of solution, the resulting curd is largely composed of soda soap formed by the reaction (in the case of stearate).

$$\begin{array}{ccccccc} \text{Sodium Chloride.} & & \text{Potassium Stearate.} & & \text{Sodium Stearate.} & & \text{Potassium Chloride.} \\ \mathrm{NaCl} & + & \mathrm{K \, . \, O \, . \, C_{18}H_{35}O} & = & \mathrm{Na \, . \, O \, . \, C_{18}H_{35}O} & + & \mathrm{KCl} \end{array}$$

In former days this reaction was utilised to prepare hard soaps in places where wood ashes only were obtainable as alkali (p. 833). Similarly, it has long been a practice to improve the softness and texture of soda soaps intended for toilet soap-making by remelting and "pearl-ashing"—*i.e.*, adding to the melted soap potassium carbonate dissolved in a little water; the rationale of which has been shown to be[1] that double decomposition takes place with formation of potash soap and sodium carbonate, thus—

$$\begin{array}{ccccccc} \text{Sodium Stearate.} & & \text{Potassium Carbonate.} & & \text{Potassium Stearate.} & & \text{Sodium Carbonate.} \\ \mathrm{2Na \, . \, O \, . \, C_{18}H_{35}O} & + & \mathrm{K_2CO_3} & = & \mathrm{2K \, . \, O \, . \, C_{18}H_{35}O} & + & \mathrm{Na_2CO_3} \end{array}$$

The presence of the potash soap makes the resulting mass less liable to crack during stamping, and also gives it better lathering qualities.

In these and all similar cases the general principle involved seems to be this:—Potassium and sodium are so related that when both alkalis are simultaneously in presence of two acids, one weaker than the other, the potash tends to unite with the stronger acid and the soda with the other. Thus when stearic and hydrochloric acids are in question, the prevailing tendency is to form potassium chloride and sodium stearate, because hydrochloric acid is the stronger acid of the two; whilst when stearic and carbonic acids are the two acids, the chief tendency is to form potassium stearate and sodium carbonate, because stearic acid is a stronger acid than carbonic acid. As in most analogous cases, however, the question of relative masses is also concerned in the result. If these be suitably chosen the actions may to some extent be reversed—*e.g.*, if a large mass of potassium chloride act on a relatively small quantity of sodium stearate, a notable amount of soft potassium stearate is formed with a corresponding quantity of sodium chloride, in opposition to the above described actions occurring when the masses of potassium and sodium salts are not widely different. Similarly, if a relatively large amount of sodium carbonate act on a small quantity of fused potash soap, a measurable amount of soda soap and a corresponding quantity of potassium carbonate are produced,

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[1] Alder Wright and Thompson, *J. Soc. Chem. Ind.*, 1885, iv., 625.

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$$\overset{\text{Sodium Chloride.}}{NaCl} + \overset{\text{Potassium Stearate.}}{K.O.C_{18}H_{35}O} = \overset{\text{Sodium Stearate.}}{Na.O.C_{18}H_{35}O} + \overset{\text{Potassium Chloride.}}{KCl}$$

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$$\overset{\text{Sodium Stearate.}}{2Na.O.C_{18}H_{35}O} + \overset{\text{Potassium Carbonate.}}{K_2CO_3} = \overset{\text{Potassium Stearate.}}{2K.O.C_{18}H_{35}O} + \overset{\text{Sodium Carbonate.}}{Na_2CO_3}$$

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In these and all similar cases the general principle involved seems to be this:—Potassium and sodium are so related that when both alkalis are simultaneously in presence of two acids, one weaker than the other, the potash tends to unite with the stronger acid and the soda with the other. Thus when stearic and hydrochloric acids are in question, the prevailing tendency is to form potassium chloride and sodium stearate, because hydrochloric acid is the stronger acid of the two; whilst when stearic and carbonic acids are the two acids, the chief tendency is to form potassium stearate and sodium carbonate, because stearic acid is a stronger acid than carbonic acid. As in most analogous cases, however, the question of relative masses is also concerned in the result. If these be suitably chosen the actions may to some extent be reversed—*e.g.*, if a large mass of potassium chloride act on a relatively small quantity of sodium stearate, a notable amount of soft potassium stearate is formed with a corresponding quantity of sodium chloride, in opposition to the above described actions occurring when the masses of potassium and sodium salts are not widely different. Similarly, if a relatively large amount of sodium carbonate act on a small quantity of fused potash soap, a measurable amount of soda soap and a corresponding quantity of potassium carbonate are produced,

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[1] Alder Wright and Thompson, *J. Soc. Chem. Ind.*, 1885, iv., 625.

notwithstanding the usual tendency to the opposite change. Thus the following figures were obtained by *Alder Wright* and *Thompson* (*loc. cit. supra*) :—

Fatty Acids Employed.	(*a*) Soda Soaps fused with K_2CO_3. Percentage of total Fatty Acids present.		(*b*) Potash Soaps fused with Na_2CO_3. Percentage of total Fatty Acids present.	
	Equivalent to the K_2CO_3 added.	Actually converted into Potash Soap.	Equivalent to the Na_2CO_3 added.	Actually converted into Soda Soap.
Stearic and oleic (tallow), .	10·4	8·0	...	...
,, ,,	45·7	34·4	...	...
,, ,,	100·0	97·95	100·0	4·3
,, ,,	104·2	99·0	1000·0	15·0
Stearic, palmitic, and oleic (palm oil and tallow),	57·2	52·1	...	...
,, ,,	108·0	90·8	177·0	9·5
Crude lauric acid (coconut oil), ...	52·8	46·4	...	...
,, ,,	114·8	87·9	197·0	6·2
Crude ricinoleic acid (castor oil), ...	50·0	48·4	...	...
,, ,,	100·0	93·8	205·0	8·2

Obviously the proportion of potassium carbonate converted into potash soap in the series (*a*) is uniformly much larger than the fraction of sodium carbonate converted into sodium soap in series (*b*)—*i.e.*, not far from the maximum possible in the first case, and only a few per cents. in the second ; showing the much stronger tendency towards the first change than towards its converse.

In similar fashion the following figures were obtained on salting out potash soaps with sodium chloride, and soda soaps with potassium chloride. In series (*a*) *m* molecules of water were used to dissolve 1 of potash soap, and *n* molecules of sodium chloride added ; in series (*b*) *m* molecules of water were added for 1 of soda soap, and *n* molecules of potassium chloride added :—

Fatty Acid Used.	*m*.	*n*.	(*a*) Potash Soaps salted out with NaCl. Percentage of Fatty Acid in Curd.		(*b*) Soda Soaps salted out with KCl. Percentage of Fatty Acid in Curd.	
			As Potash Soap.	As Soda Soap.	As Potash Soap.	As Soda Soap.
Stearic and oleic acids (tallow),	100	5	10·5	89·5	79·1	20·9
,, ,, ,,	200	20	5·1	94·9	82·1	17·9
Stearic, palmitic, and oleic (palm oil and tallow), .	200	20	3·8	96·2	95·8	4·2
Crude lauric acid (coconut oil), ...	200	20	5·4	94·6	74·8	25·2

Here the disproportion between the results in the (*a*) series and those in the (*b*) series is much less than in the case of carbonates, although it is still obvious that on the whole there is a greater tendency for sodium chloride to form a soda soap by acting on a potash soap than for the converse reaction to occur.

The same result follows if a mixture of equivalent quantities of potash and soda soaps (obtained by halving the fatty acids, and neutralising one-half with one alkali, and the other with the other) be dissolved in water and salted out with a mixture of equivalent quantities of potassium and sodium chlorides. A much larger proportion of soda soap is thus separated than is equivalent to the potash soap simultaneously thrown out of solution, the precise proportion varying with the nature of the fatty acids. Thus the following figures were obtained, indicating from 1·6 to 5·7 molecules of soda soap to 1 of potash soap:—

Fatty Acid Used.	Percentage of Fatty Acid contained.		Molecular Ratio of Soda Soap to Potash Soap.
	As Potash Soap.	As Soda Soap.	
Pure oleic acid,	38·0	62·0	1·63 to 1
Crude ricinoleic acid (from castor oil),	17·8	82·2	4·6 to 1
Stearic, oleic, and rosin acids mixed (primrose soap),	17·2	82·8	4·8 to 1
Crude lauric acid (from coconut oil soap),	15·1	85·9	5·7 to 1

It is remarkable that when only one acid is present, or a mixture of organic acids not greatly differing in strength, the proportion of soda and potash soaps formed by acting on a mixture of the two bases is sensibly the same as the proportion of the bases; thus with equal molecular quantities of potash and soda, and amounts of acid exactly equivalent to either of the alkalis separately, or to one-half of the two jointly, the following figures were obtained:—

Fatty Acids Employed.	Percentage of Total Fatty Acid converted into	
	Soda Soap.	Potash Soap.
Pure stearic acid,	51·2	48·8
,, oleic acid,	50·8	49·2
Crude stearic and oleic acids (tallow),	51·5	48·5
,, stearic, palmitic, and oleic acids (palm oil and tallow),	48·2	51·8
,, lauric acid (coconut oil),	49·7	50·3
Mean,	50·3	49·7

In similar fashion, if a soda soap be melted and well intermixed with just as much potassium hydroxide as is chemically equivalent to the soda present, or if a potash soap be similarly treated with the equivalent amount of sodium hydroxide, the result in either case is the formation of a mixture of potash and soda soaps in practically equivalent quantities.

ANALYSIS OF SOAPS.

The general composition and character of soaps of different kinds being subject to considerable variation, the analytical determinations most useful in certain cases are not always those most valuable in other instances. Thus in the case of a fulling or wool-scouring soap, freedom from excess of alkali or from alkaline salts (silicate, etc.) that might act injuriously on the wool fibre is the most important point, together with the proper nature of the fatty matters employed; whilst in the case of a laundry soap, freedom from excess of alkali is not at all an important condition, the presence of certain kinds of alkaline material (more especially alkali carbonates) being generally beneficial rather than otherwise, *cæteris paribus*.

In all cases, however, a highly important consideration is the proportion of actual soap present—*i.e.*, the proportion of the alkali salts of fatty and resinous acids, apart from other saline matters, uncombined alkalis, unsaponified glycerides, water, glycerol, and substances added to give weight, or to increase the stiffness or the detergent action, or for other reasons.

An examination of the fatty acids set free on decomposition with a mineral acid is often useful, as giving information as to the nature and quality of the fatty matters originally employed; the first results being corrected, when necessary, by determining the amount of unsaponified fat present, and also the amount and general nature of unsaponifiable constituents, such as cholesterol, hydrocarbons, etc. Moreover, with certain kinds of medicated and disinfected soaps the amount of active ingredient incorporated therein requires determination.

When the amount of total alkaline matter present (soda, or potash, or both) is known, expressed as anhydrous oxide (Na_2O, or K_2O), and also that portion which is "free"—*i.e.*, not combined with fatty and resinous acids—the difference obviously represents the combined alkali contained as actual soap; *i.e.*, if the percentage of "total alkali" (expressed as Na_2O) be a, and that of "free alkali" $= b$, $a - b$ is the percentage of "combined alkali." Similarly if c be the percentage of crude fatty acids, etc., obtained on decomposition with a mineral acid, whilst d is the percentage of unsaponified grease and unsaponifiable matters present therein admixed with the pure fatty acids, $c - d$ is the percentage of fatty acids present in combination as soap. The weight of actual soap present then is $a - b + (c - d) - n$ per cent., where n is the amount to be subtracted in order to calculate fatty acids into fatty anhydrides (the soap being viewed for present purposes as being made up of compounds of metallic oxides and the anhydrides of acids, such as Na_2O, $(C_{18}H_{35}O)_2O$ for sodium stearate, and so on). Obviously, if the alkali be expressed as Na_2O, $n = \frac{9}{31}(a - b)$; whilst if it be expressed as K_2O, $n = \frac{9}{47{\cdot}1}(a - b)$; so that in the first case the percentage of actual soap is—

$$a - b + (c - d) - \frac{9}{31}\ (a - b) = \frac{22}{31}(a - b) + (c - d),$$

and in the second case—

$$a - b + (c - d) - \frac{9}{47{\cdot}1}(a - b) = \frac{38{\cdot}1}{47{\cdot}1}(a - b) + (c - d).$$

For instance, suppose that a soda soap gave the following results on analysis—

Crude mixture of fatty acids, etc.,	=	c	=	67·05 per cent.
Unsaponifiable matter, etc., .	=	d	=	1·80 ,,
Fatty acids present in soap,	=	$c - d$	=	65·25 ,,
Total alkali (expressed as Na_2O), .	=	a	=	8·55 ,,
Free alkali ,, .	=	b	=	0·85 ,,
Combined alkali present in soap,	=	$a - b$	=	7·70 ,,

Hence— $$n = \frac{9}{31} \times 7{\cdot}70 = 2{\cdot}23.$$

Whence the fatty anhydrides are 65·25 — 2·23 = 63·02
And the actual soap present = 63·02 + 7·70 = 70·72

The analysis would then be stated thus—

Fatty anhydrides, . .	63·02 per cent.	Jointly = 70·72 per cent. of actual soap.
Combined alkali (Na_2O), .	7·70 ,,	
Unsaponifiable matter, etc.,	1·80 ,,	
Water, free alkali, saline matters, etc. (by difference), ...	27·48 ,,	Containing free alkali equivalent to 0·85 per cent. Na_2O, or $\frac{0{\cdot}85}{7{\cdot}70}$ = about $\frac{1}{9}$ of the combined alkali.
	100·00	

In order, therefore, to determine the percentage of actual soap present, the four quantities a, b, c, and d must be determined; during the course of which analysis, the separate percentages of potash and soda may conveniently be also determined (when the two alkalis are simultaneously present). Moreover, whilst c and d are being separated from one another, the respective amounts of unsaponified glycerides and of unsaponifiable matter present in d may be conveniently determined, and further examinations made as to the characters of the separated and purified fatty acids, $c - d$, and of the unsaponifiable matter. In particular the proportion of rosin acids in the former may be determined, as also the melting point, etc., so as to obtain information as to the probable nature of the fatty matters used. This last point, however, is one where analytical data, as such, often fails to give satisfactory results—*i.e.*, the inspection of the mixed fatty acids and the valuation of their melting points, etc., often leads to nothing definite; in some cases, however, the application of other tests (qualitative or quantitative) leads to useful results—*e.g.*, the elaidin test, etc.

The average molecular weight, E, of the fatty acids contained in the soap is frequently a datum of considerable value; this is readily deduced when *a*, *b*, *c*, and *d* are known, as shown on p. 239, being given by the equation—

$$E = \frac{c-d}{a-b} \times 31, \text{ when the alkali is expressed as } Na_2O,$$

$$E = \frac{c-d}{a-b} \times 47{\cdot}1 \quad ,, \quad ,, \quad ,, \quad K_2O.$$

Thus, in the above example, the value of E is—

$$\frac{65{\cdot}25}{7{\cdot}70} \times 31 = 263.$$

When required, the proportion of water present in the soap may be directly determined, as also any other constituents present, such, for example, as admixed weighting substances of mineral or organic nature (China clay, steatite, starch, sand, bran, etc.); saline matters (sodium chloride, sulphate, etc.); silica (from sodium silicate); glycerol; sugar; and so on.

In order to carry out a complete detailed analysis, the following methods of procedure have been found convenient by the author[1] (*A. W.*), the exact selection to be made varying with circumstances:—

Water.—A convenient weight of *an average sample* of the soap cut up into thin shavings is dried, first at a temperature somewhat below 100° C. so as to avoid fusion, finally at 110° to 120° C. The loss of weight may be taken as water, especially when other volatile substances (carbolic acid, essential oils, etc.) are absent or present in small quantities only.

For many purposes this direct determination is one of the most important valuations, especially in conjunction with an estimation of free alkali (*e.g.*, in the case of soft soap). In other cases the direct determination is quite unnecessary, more particularly when the amount of actual soap present is determined, water and saline matters being conveniently taken by difference.

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[1] Various more or less similar methods and processes have been put forward by other chemists—*e.g.*, C. Hope, *Chemical News*, 1881, xliii., 219; Filsinger, *Chem. Zeit.*, April, 1884; Allen, *Commercial Organic Analysis*, Second Edition, vol. ii., 251; Leeds, *Chemical News*, 1885, xlviii., 166; Alder Wright and Thompson, *Analyst*, 1886, xi., 44; Spaeth, *J. Soc. Chem. Ind.*, 1896, xv., 139; Moreschini, *ibid.*, 1897, xvi., 831; Hefelmann and Steiner, *ibid.*, 1898, xvii., 496; Huggenberg, *ibid.*, 496; Henriques and Meyer, *ibid.*, 1900, xix., 857; etc.

Watson Smith's Method.—Instead of reducing the soap to thin slices and drying without fusion, the amount of water may be arrived at by heating 5 or 10 grammes in a large porcelain crucible set in a sand-bath, and stirring with a bit of glass rod (weighed with the crucible) until no more dew is deposited on a piece of glass placed over the crucible (the lamp being removed). When this stage is reached the water is practically all expelled, and a nearly constant weight attained. Care must be taken not to overheat and burn the soap; the glass rod should have a rough jagged end to facilitate the breaking up of clots.[1]

J. A. Wilson recommends [2] weighing out about 2·5 grammes of soap in a dish and dissolving it in about 5 c.c. of absolute alcohol by means of heat. About 10 grammes of ignited sand are then added and the whole evaporated to dryness. The residue is again treated with 5 c.c. of absolute alcohol and evaporated, and finally dried at 100° to 105° in an air-bath. The addition of the sand facilitates the expulsion of water with the alcohol, and renders it more easy to treat the dried soap in a Soxhlet apparatus for dissolving out unsaponified fat, etc.

Unsaponified Fat, Hydrocarbons, Spermaceti, Wax, etc.—Five (or preferably 10) grammes of soap are dried, first at 100° or below, and finally at 120° C.; or in a crucible, or with alcohol and sand as above. The residue is exhausted in a Soxhlet tube with light petroleum spirit; or digested with successive small quantities of the solvent, each portion being decanted (if necessary through a filter) until all fat, etc., has been dissolved. Ether may also be used, but is more apt to dissolve soap.

The residue left on evaporation of the solvent may be examined as to its physical properties, and the saponifiable portion determined by heating the mass with excess of standard alcoholic potassium hydroxide, precisely as in determining the saponification value of an oil or fat, and titrating the unneutralised alkali when saponification is complete.

The exactly neutral fluid is then evaporated and the residue again treated with light petroleum spirit so as to dissolve out hydrocarbons, cholesterol or other alcoholiform saponification products, etc., obtained by evaporating the extract; whilst the undissolved portion on acidification and shaking with ether enables the fatty acids, etc., produced by the saponification to be isolated for examination.

In cases where a full examination of the unsaponified fat, etc., is required, it is preferable to employ a larger quantity (50 or even 100 grammes) of soap, and not to combine this determination with that of water, etc., lost by drying.

As a rule, little but unsaponified glycerides are thus extracted; but "oleine" soaps often contain a small percentage of hydrocarbons contained in the oleine (distilled, p. 367), whilst if wool grease has been used to adulterate tallow, notable amounts of cholesterol, etc., may be present. Spermaceti, vaseline, etc.,[3] may be present in special kinds

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[1] *J. Soc. Dyers and Colourists*, i., 31.

[2] *Chemical News*, 1892, lxvi., 200.

[3] When wax is present, toluene dissolves it out in the Soxhlet tube better than petroleum spirit (*Schnaible*).

of toilet soap; whilst certain laundry soaps are purposely intermixed with paraffin oil and similar hydrocarbons.

The unsaponified fat, etc., may also be isolated by dissolving the soap (which need not be dried) in hot alcohol and slightly diluting the solution with water. Before the liquid is completely cool, a little ether is introduced (care being taken that no light is near to inflame ether vapour), which will generally prevent the mass gelatinising. After the addition of more ether the whole is well agitated, and if separation does not occur, more water is added, the ethereal solution being finally drawn off by means of a separating funnel or Chattaway's tube (p. 170).

The ethereal extract thus obtained usually contains soap, so that it should be evaporated and the residue dissolved in petroleum spirit and filtered. It often requires considerable manipulation to get the alcohol, ether, and water in the right proportions to bring about a proper separation into two fluids, one an aqueous alcoholic soap solution, the other an ethereal solution of fat, etc.

Fatty Anhydrides and Total Alkali.—The residue deprived of fat, etc., by petroleum spirit left in the Soxhlet tube as above, is dissolved in water[1] and decomposed by boiling with a slight excess of standard acid. On standing and cooling, the fatty acids separate as a cake, which is washed, dried, and weighed,[2] and then subjected to such further tests as may be deemed necessary (melting point, elaidin test, etc.), more especially rosin acid determination (*infra*).

If the fatty acids are very soft, or are derived from coconut or palm-kernel oil, a known weight (5 or 10 grammes) of beeswax or paraffin wax may be advantageously added before cooling so as to form a more solid cake, and to assist in dissolving out from the water the more soluble acids, due correction being made for the weight of added substance. This, however, obviously prevents any physical or other examination of the fatty acids after their being separated from the soap.

If such an examination is not required it often saves time to weigh

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[1] If mineral substances, etc., insoluble in alcohol are present, the soap may be treated (conveniently still in the Soxhlet tube) with alcohol, so as to dissolve out the soap, and leave the insoluble substances. In this case drying without addition of sand, etc., is preferable. The alcoholic extract may be evaporated to dryness and the residue weighed, so as directly to determine the "actual soap" present; or it may be diluted with hot water and treated with excess of standard acid, etc.

[2] Or the hot fluids may be washed into a separating funnel, the aqueous part run off, and the fluid fatty acids washed out on to a wet filter as in determining the Hehner value of an oil, etc. If particles of fatty acid adhere to the vessels either in this mode of operating or with the solid cake, they should be washed off with a little ether, etc., into a small beaker or basin, and the solvent evaporated, the rest of the fatty acids being subsequently added, and the whole weighed together after drying. When the soap contains any considerable amount of soluble fatty acids (*e.g.*, when made from mixtures containing coconut or palm-kernel oil) these partly remain in the aqueous liquor, from which they may be, for the most part, extracted by shaking with ether.

out a separate amount of average soap (10 grammes [1]) and without drying or treating with petroleum spirit to dissolve this in water, decompose with acid, and weigh the resulting mixture of fatty acids, unsaponified fat, etc., correcting the results by means of a separate determination of the latter quantity. The corrected percentage of fatty acids is calculated to fatty anhydrides as above described (p. 852).

When *nitric* acid is used as the standard acid, and the alkali employed for back-titration [2] is free from chloride and sulphate, the neutralised acid may be divided into two halves for the determination of *sulphate* and *chloride* respectively; or, if required, a portion may be reserved for glycerol determination (*infra*).

From the amount of standard acid used, less that titrated in the liquid after removal of fatty acids, the total quantity of alkali present is known, including that present as soap, that contained as hydroxide or carbonate, and that present as other inorganic salts of alkaline reaction—*e.g.*, silicate.

Free Alkali.—The term "free alkali" is generally understood as including the alkalinity of all substances present in soap possessing an alkaline reaction—*i.e.*, the sum of the alkalinity due to hydroxide (caustic alkali), carbonate, and other salts such as silicate; so that the difference between the "total alkali" and the "free alkali" exactly represents the alkali combined with fatty and resinous acids as actual soap.

Excepting in the case of freshly made soap, especially when preserved in large-sized blocks, but little caustic alkali is ever found in commercial soap, because the absorption of carbon dioxide from the air is tolerably rapid; but the passage of that gas into the interior of a large mass, and to a less extent into the centre of an ordinary bar, is by no means instantaneous, so that the interior portion of a comparatively freshly made curd or hydrated soap (pp. 822, 831) often contains a notable amount of hydroxide.

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[1] Instead of using 10 grammes of soap, a smaller quantity, say 2 grammes, may be dissolved in water, acidified, shaken with ether in a well-closed vessel, and the ethereal solution separated and evaporated. This method is preferable with soaps made from coconut and palm-kernel oils on account of the partial solubility of the fatty acids thence derived in water. In order to avoid loss of volatile acids during drying, the ethereal solution may be exactly neutralised with alcoholic solution of pure sodium hydroxide, evaporated to complete dryness and weighed. By subtracting the Na_2O contained in the alcoholic sodium hydroxide from the weight of the pure soap (together with unsaponified grease and unsaponifiable matters) thus obtained, the weight of fatty anhydrides + unsaponified grease and unsaponifiable matters is known. The soda thus neutralised is the "combined alkali" (*vide infra*, "fatty acid titration test" for free alkali).

[2] Cochineal is a convenient indicator for the purpose. If any soluble organic acids are present in the aqueous fluid, they may be approximately estimated by first titrating with methyl orange as indicator, the colour change occurring when all the mineral acid present is neutralised; and then going on with addition of phenol-phthalein, which is not reddened till the organic acids are neutralised. The additional alkali thus consumed may be calculated as *valeric acid*, $C_5H_{10}O_2$, in the case of soaps containing whale oils; or as *heptoic acid*, $C_7H_{14}O_2$, or *octoic acid*, $C_8H_{16}O_2$, in the case of coconut oil soaps.

Alcohol Test.—In order to distinguish the free alkali present as hydroxide from that contained in other forms, *C. Hope*[1] dissolves a known weight of an average sample in strong alcohol and filters the liquid. Carbonate, silicate, etc., are left on the filter; whilst caustic alkali (whether potassium or sodium hydroxide) passes through, dissolved in the alcohol with the neutral soap.

The operation may be conveniently carried out in the following manner:—5 grammes of the undried average sample of soap are dissolved in hot alcohol (free from all acidity or alkalinity, and as strong as possible) and the solution filtered through a hot water funnel. The undissolved residue is thoroughly washed with alcohol, then treated with water, and the alkalinity determined. As a general rule, the alcoholic filtrate is neutral, but sometimes it is faintly acid to phenolphthalein.

Apparently with a slightly moist soap mass, absorption of carbonic acid from the air tends to develop a trace of "acid soap" (pp. 26, 847) with a corresponding quantity of alkali carbonate. As this latter is undissolved by the alcohol it does not react on the acid soap during solution so as to neutralise it again.[2] In such a case the acidity ("negative alkalinity") of the alcoholic solution is determined, and the amount subtracted from the positive alkalinity of the residue. Thus 5 grammes of soap gave an alcoholic solution in which the acidity represented 0·25 c.c. of semi-normal alkali; whilst the residue neutralised 0·6 c.c. of semi-normal acid: hence the "free alkali" is reckoned as 0·6 − 0·25 = 0·35 c.c. of semi-normal acid corresponding with 0·0054 gramme of sodium oxide (Na_2O) or 0·108 per cent.

Sometimes, on the other hand, the alcoholic filtrate is more or less alkaline (through the presence of hydroxide in the soap); in which case the amount of alkali present in the filtrate is determined (with phenol-phthalein as indicator) and *added* to that found in the residue, this method of operating being "Hope's test" in its original form.

In a method devised by *Divine*[3] the total free alkali is determined by mixing an alcoholic solution of the soap with an excess of a decinormal solution of stearic acid, and titrating the excess with standard alkali. The caustic alkali is found by precipitating the carbonate with barium chloride, and titrating the filtrate with the standard stearic acid solution.

It has been pointed out by *Wilson*[4] that when caustic alkali is present in a soap which also contains unsaponified glycerides, the alcoholic alkaline solution is apt to act on these glycerides, diminishing the alkalinity by saponifying them, and so causing the amount of free alkali to be understated. The author has found that this source of

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[1] *Chemical News*, 1881, xliii., 219.

[2] With some kinds of soap, if a stream of pure carbon dioxide be passed through a hot clear filtered alcoholic solution of the soap, a slight visible precipitation of alkali carbonate results, together with the formation of an equivalent amount of "acid soap."

[3] *J. Amer. Chem. Soc.*, 1900, xxii., 639.

[4] *Chemical News*, 1889, lix., 280.

error is readily avoided by cutting the soap to be examined into very thin slices or shavings, and exposing these loosely piled together in a small dish or beaker to the action of carbon dioxide, conveniently by placing the dish in a wide-mouthed bottle filled with the gas, loosely corking it, and leaving the whole till next day. By that time all caustic alkali is carbonated, so that the alcohol test can be applied without any error due to saponification of glycerides, due correction being made, if necessary, for the " negative alkalinity " of the alcoholic filtrate caused by the action of the carbon dioxide forming small quantities of acid soap and alkali carbonate. This mode of operating, however, obviously does not enable a distinction to be made between the relative amount of alkali present as hydroxide and carbonate.

In the case of strongly alkaline soaps where a slight amount of error in determining the total amount of free alkali is not material, two other tests are applicable, respectively designated the " fatty acid titration test " and the " salting out test."[1]

Fatty Acid Titration Test.—This consists in determining the total alkali as above, separating the fatty acids, and titrating them, reckoning the difference as free alkali. In practice the unavoidable experimental error of this differential method is sometimes found to be sufficiently great to render the determination of minute quantities of free alkali decidedly uncertain, so that for nearly neutral soaps the method is useless. Moreover, the fatty acids separated by the action of dilute aqueous acid on soap are sometimes partially soluble in water, so that although the insoluble acids largely dissolve the soluble ones and bring them out of solution in water into the supernatant layer of melted fatty acids (as ether would dissolve out similar matters from an aqueous solution), still a small proportion of the soluble acids is apt to be retained by the water and lost, thus tending to increase unduly the value of the free alkali determination. This is especially noticeable when coconut, or palm-kernel oil has been employed in making the soap. When, however, the free alkali is large, so that a small degree of possible error in its determination is not of great importance, this method is very convenient.

The " salting out test " consists in dissolving a weighed quantity of soap in hot water, adding salt so as to throw the curd out of solution, filtering it off, and titrating the alkali in the filtrate. This may be conveniently done in two fractions, one being titrated directly so as to obtain the *total* alkali present (caustic + carbonated); the other treated with barium chloride in excess, and the *caustic* alkali determined in the filtrate from the barium carbonate, etc., thus precipitated (*vide* footnote, p. 780).

Apart from deficiency of the caustic alkali value due to unavoidable absorption of carbon dioxide from the air during the operations, a source of error in excess is that hydrolysis of the soap examined necessarily takes place to an extent which varies with the temperature, the quantity of water present relatively to the soap, the nature of the

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[1] Alder Wright and Thomson, *J. Soc. Chem. Ind.*, 1885, iv., 625.

fatty acids present, and the amount of free alkali. When, however, a uniform mode of manipulating is adhered to, the results obtained with a given kind of soap are comparable amongst themselves, so that the figures are often of considerable practical use, especially when corrected (by means of carefully made tests using the alcohol process) so as to get an approximate valuation of the excess of alkali due to the hydrolytic action.

For instance, the following figures represent the difference in amount of free alcohol found with a variety of soaps according as the alcohol test (A. T.) or salting out test (S.O.T.) was used; the numbers are reckoned per 100 parts of alkali combined with fatty acids as soap—*i.e.*, if the combined alkali = 10·0 and the free alkali = 0·52 per 100 of soap, this would correspond with 5·2 parts of free alkali per 100 of combined alkali :—

Nature of Soap Used.	A.T.	S.O.T.	Excess of S.O.T. over A.T.
Pure coconut oil soap, not strongly alkaline, ...	5.0	9·1	4·1
Another sample of ditto, ...	2·8	5·8	3·0
A British toilet soap, largely made from coconut oil, ...	1·3	5·8	4·5
A foreign toilet soap, largely made from coconut oil (neutral), ...	0	3·5	3·5
A high-class American toilet soap, . .	1·8	5·4	3·6
A toilet soap largely made from lard (neutral), ...	0	3·2	3·2
A second-class ditto, chiefly made from tallow, ...	1·9	4·8	2·9
A cotton-seed oil soap, ...	7·2	9·8	2·6
A tallow rosin (primrose), . . .	1·1	3·0	1·9
A neutral castor oil soap, . . .	0	1·7	1·7
A bleached palm oil soap, . . .	5·0	6·4	1·4
A tolerably alkaline curd soap, . .	18·3	18·3	0
Pure stearic acid soda soap (neutral), .	0	0·7	0·7

When the aqueous soap solution is tolerably concentrated (about 1 part by weight of actual anhydrous soap to 10 of water), and the soap itself contains a good deal of free alkali, the error due to hydrolysis becomes small enough to be quite negligible; but with a nearly neutral soap the hydrolytic error becomes several times as large as the free alkali actually present.

Robertson[1] has shown that in determining the amount of caustic and carbonated alkali by "salting out" the soap with sodium chloride, titrating the liquid with phenol-phthalein as indicator, and finishing the titration with methyl orange as indicator, the salt has a considerable influence upon both indicators, so that the apparent amount of caustic alkali is too high, and that of the carbonated alkali too low.

In determining the free alkali with methyl orange as indicator, a

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[1] *J. Soc. Chem. Ind.*, 1901, xx., 936.

deduction of 0·0114 c.c. of deci-normal sulphuric acid must be made for each gramme of sodium chloride used, or of 0·004 for each c.c. of a saturated solution of sodium chloride.

The exact correction to be applied in titrating caustic and carbonated alkali together was found to vary with the different proportions of each; but sufficiently accurate results were obtained by adding 0·024 c.c. to the amount of deci-normal sulphuric acid for each c.c. of saturated sodium chloride solution when titrating with phenol-phthalein as indicator, and deducting 0·0285 when using methyl orange.

The first titration gives the caustic alkali and half of the carbonate, and the second the remainder of the carbonate.

Potash and Soda.—When both alkalis are present, and it is required to determine their relative amount, several methods of analysis are available. One of the simplest is to decompose a known quantity of soap with dilute hydrochloric acid, evaporate down the aqueous filtrate, convert potassium chloride into platino-chloride, and weigh this.

In the absence of more than minute quantities of sulphate, silicate, etc., the mixed alkali chloride solution may be evaporated down and weighed, the chlorine contained determined (volumetrically or otherwise), and the ratio of potassium to sodium calculated from the indirect results.

The soap may also conveniently be charred and the alkalis dissolved out from the ash for treatment. When much sulphate is present the alkalis should be weighed as sulphates and the indirect determination made by determining the barium sulphate yielded by the mixture.

Application of the Polenske Method to Soap Analysis.—*Fryer*[1] has shown that the Polenske method (pp. 244, 659) is of considerable value in the analysis of soaps prepared from coconut and palm-kernel oils:—Five grammes of the separated and filtered fatty acids are heated in the flask of the standard apparatus with 2 c.c. of 50 per cent. sodium hydroxide solution until the liquid clarifies. The soap mixture is then cooled somewhat, and diluted with 100 c.c. of boiling water, and, after the addition of 0·1 gramme of powdered pumice stone, the soap is decomposed with 40 c.c. of 6 per cent. sulphuric acid. The flask is then connected with the condenser, heated gently until the fatty acids melt, and 110 c.c. of the liquid distilled in 19 to 21 minutes. The distillate is cooled to 15° C. and filtered, and the filtrate and alcoholic washings from the condenser tube are titrated with $\frac{N}{10}$ alkali.

The average figures obtained for the "insoluble" volatile fatty acids from coconut oil soap were 17·3 per cent., whilst palm-kernel oil soap fatty acids gave 10·5 per cent.

Rosin Acids.—It is often of considerable importance to determine with some degree of approximate accuracy the proportion between the rosin acids and the ordinary fatty acids present in a given sample of soap. Several older methods have been proposed, none of which yield very accurate results; but two processes have been introduced of a somewhat more satisfactory nature, although still leaving a good deal to be desired.

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[1] *J. Soc. Chem. Ind.*, 1918, xxxvii., 262 T.

Gladding's Method.—The earlier of these methods is that of *Gladding*,[1] based upon much the same principle as the methods of separating liquid and solid fatty acids—viz., conversion into metallic salts, one soluble in ether, the other insoluble. The soap to be tested is freed from unsaponified fat, etc., by treatment with petroleum spirit; or, if glycerides only are present, by heating with strong alcohol and a few drops of alcoholic potassium hydroxide in excess of the amount required to effect complete saponification.

The alcoholic soap solution is then agitated with powdered neutral silver nitrate and ether in a closed vessel for some time (0·5 grm. fatty acid, 1 grm. silver nitrate, and 100 c.c. of ethereal fluid altogether, answer well); after some minutes shaking flocculent silver stearate, etc., subsides, whilst silver resinate remains dissolved. A known fraction of the ether is siphoned off or removed by means of a "Chattaway tube" (p. 170), and shaken with dilute hydrochloric acid, whereby the silver is removed and an ethereal solution of rosin acids produced. This is evaporated, and the residue of rosin acids weighed. Finally, a correction is made for the solubility of silver oleate, etc., amounting to a subtraction from the weight of rosin acids obtained of 23·5 milligrammes per 100 c.c. of ether.

A notable source of error in this method lies in the uncertainty of this correction, inasmuch as somewhat widely different values are obtained with different acids—*e.g.*,[2]

Nature of Fatty Matters in Soap Examined.	Fatty Substances Dissolved (as Silver Salt) in 100 c.c. of Alcoholic Ether.		
	Maximum.	Minimum.	General Average.
	Milligrammes.	Milligrammes.	Milligrammes.
Pure stearic acid,	16·0	8·0	11·6
,, oleic ,,	15·0	9·0	12·0
Nearly pure palmitic acid,	30·0	28·0	29·1
Cotton-seed oil,	34·0	20·0	26·9
Castor oil,	62·0	49·0	53·9
Coconut oil (fatty acids dried on water-bath),	17·5	12·0	14·8
Coconut oil (fatty acids dried over H_2SO_4),	23·0	19·0	21·1
Stearic and oleic acids, in nearly equal proportions,	22·0	18·0	19·1
Stearic acid and cotton-seed oil, in nearly equal proportions,	...	...	25·5
Oleic acid and cotton-seed oil, in nearly equal proportions,	...	...	24·5
Stearic acid and cocoa-nut oil (water-bath), in nearly equal proportions,	...	...	23·4
Oleic acid and coconut oil (water-bath), in nearly equal proportions,	...	...	25·6

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[1] *Chemical News*, 1882, xlv., 159.

[2] Alder Wright and Thompson, *Proc. Chem. Soc.*, 1886, 175; also *Chemical News*, 1886, liii., 165.

According to the nature of the fatty acids, the correction may thus vary between 8 and 62 milligrammes in the most extreme cases, and between 11·6 and 53·9 for average values, these quantities representing on 500 milligrammes of fatty acids respectively 2·3 and 10·8 per cent.; so that whilst 23·5 milligrammes (= 4·7 per cent.) is not far from a mean value, it is by no means equally applicable in all cases.[1]

Twitchell's Method [2] depends on the property of ordinary fatty acids to form compound esters when dissolved in alcohol and treated with hydrochloric acid gas. If the alcohol be absolute and the solution saturated with the gas, the conversion is practially complete with fatty acids, whereas rosin acids are not acted upon at all; with alcohol of only 90 per cent., however, the action is not complete, several per cents. of the fatty acids escaping conversion. In carrying out this method, from 2 to 3 grammes of the mixed acids are dissolved in 10 volumes of absolute alcohol, and dry hydrochloric acid gas passed through the solution for 45 minutes, the vessel being cooled by immersion in water, with the result that the fatty esters presently separate and float on the surface.

After standing for half an hour the mixture is diluted with five times its volume of water and boiled till clear, the esters and rosin acids floating on the top. The whole is then shaken with about 50 c.c. of light petroleum spirit; and after separation, the hydrocarbon solution is washed by shaking with water, and finally shaken with 5 c.c. of alcohol and 50 c.c. of water containing 0·5 gramme of potassium hydroxide.

The alkali dissolves out the rosin acids from the hydrocarbon, leaving the fatty ester still dissolved therein; on separation of the aqueous solution of resinate, and agitation with ether or petroleum spirit after acidification, the rosin acids are obtained in solution, and may either be weighed (after evaporation to dryness) or titrated,

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[1] *Lewkowitsch* subsequently found still wider discrepancies between the corrections necessary in the case of stearic and oleic acids—*e.g.*,

	Correction per 100 c.c. of Alcoholic Ether.
Oleic acid,	109·0 to 109·4 milligrammes.
Stearic acid,	5·4 to 5·8 „

(*J. Soc. Chem. Ind.*, 1893, xii., 503).

Hübl and *Stadler* modify Gladding's process by precipitating the mixed silver salts from the largely diluted soap solution by means of aqueous silver nitrate, drying, and dissolving out silver resinate with ether in a Soxhlet tube. *Grittner* and *Szilazi* add alcoholic calcium nitrate solution to the alcoholic soap solution to be tested, so as to remove most of the stearate, palmitate, and oleate present by precipitation: the filtrate is then treated with silver nitrate and ether as in Gladding's process. According to *Lewkowitsch* (*loc. cit. supra*) neither modification gives satisfactory results, the quantity of rosin found being generally *below* that actually present when soap made from known mixtures of fatty matters and rosin are examined as test samples. On the other hand, the figures obtained by means of Gladding's original process are generally *several per cents. too high*, even when the correction to be used has been separately determined for the particular fatty acids, etc., used for the test samples employed.

[2] *Analyst*, 1891, xvi., 169; also *J. Soc. Chem. Ind.*, 1891, x., 804.

assuming some particular value for their mean equivalent.[1] If glycerides are present in the fatty acid mixture, this does not in any way invalidate the rosin determination, as the glycerides are not dissolved out by the alkaline liquor together with the rosin acids.

Evans and *Black*[2] have made a systematic study of Twitchell's method, and have found that by leaving the alcohol, after saturation with hydrochloric acid and before dilution with water, all night upon the hot water-bath, the results obtained are considerably lower than in the ordinary method.

Since the volumetric method is sufficiently accurate when the molecular equivalent of the rosin is known, they have made the attempt to separate the rosin in a given sample, determine its molecular equivalent, and use this number as the factor in the determination.

In test experiments somewhat discordant results were obtained, which were attributed to the loss that occurred in the separation of the rosin.

Fortini's Method.—As was pointed out above, Twitchell's method has the drawback of indicating an apparent small proportion of rosin when none is present, whilst it is not applicable to resins other than colophony. These drawbacks are obviated, in a method devised by *Fortini*,[3] which is based upon the fact that resin acids form nitro-derivatives which are insoluble in petroleum spirit.

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[1] Test experiments made by *Twitchell* showed that when the value 346, found as the mean equivalent weight of a sample of colophony, was used to calculate the result of titration of the rosin acids isolated from known mixtures of that colophony and fatty acids, the titration values always came out higher than those found by weighing; thus—

	Volumetric.	Gravimetric.
	21·40	..
	20·36	..
	19·91	..
Average,	20·56	18·93

Hence apparently from 1 to 2 per cent. of constituents were present, which were not of acid nature, and, consequently, not dissolved by the potassium hydroxide solution, and, therefore, not ultimately weighed with the true rosin acids. Such constituents would be weighed together with the rosin acids isolated by Gladding's process. *Lewkowitsch* finds (*J. Soc. Chem. Ind.*, 1893, xii., 505) that the mean equivalent of different samples of commercial rosin varies within somewhat wide limits. Thus, with six samples of American rosin values were found varying between 340·8 and 364, with an average of 348·3. Hence, the percentage of rosin found by titration can only be regarded as a somewhat rough approximation. On the other hand, Twitchell's process, applied to pure stearic acid and other fatty acids and mixtures free from rosin, indicated from 1·07 to 3·67 per cent. of that substance, the products obtained being weighed; whence it would seem that the quantity of rosin apparently found in a given sample of soap by Twitchell's process would be too high, and that a correction should be made to allow for this source of error (probably incomplete conversion of fatty acids into compound esters, or subsequent decomposition of compound esters). In practice, however, the quantity of rosin actually found is generally somewhat *below* that known to be present when test samples of known composition are examined.

[2] *Amer. Chem. J.*, 1895, xvii., 59.

[3] *Annali Chim. Applic.*, 1918, ix., 102.

Twenty grammes of the soap are dissolved in 100 c.c. of hot water, and the fatty and resin acids liberated by the addition of sulphuric acid, washed with hot water, and dried for about thirty minutes at 100° C., if necessary, in a current of carbon dioxide.

Two grammes of the mixed acids are dissolved in 50 c.c. of petroleum spirit, boiling at 40° to 70° C., in a separating funnel, and the solution treated with successive small portions of 10 c.c. of nitric acid, prepared by mixing 25 c.c. of fuming nitric acid (sp. gr. 1·52) with 75 c.c. of strong nitric acid (sp. gr. 1·48), and treating the mixture with a few crystals of urea to destroy nitrous acid.

The liquid is shaken for two to three minutes and allowed to stand until the two layers separate. The acid layer is drawn off, and the treatment is repeated with 5 c.c. of the nitric acid, which is drawn off in turn, and the residual ethereal solution is washed first with ordinary nitric acid, then with water, and filtered, the filtrate is evaporated at a low temperature, and the residue of fatty acids dried and weighed.

The resin acids, which have been converted into nitro-derivatives insoluble in petroleum spirit, are separated with the acid layer.

In the presence of oleic acid the results for the fatty acids are a little too high, but even then will be within 1 per cent. of the theoretical amount in the case of mixtures containing from 5 to 20 per cent. of resin.

Sodium Silicate.—The substance left undissolved by alcohol in the determination of free alkali by the "alcohol test" (*supra*), after treatment of water and filtration, may be titrated for alkalinity and then evaporated to dryness with a slight excess of hydrochloric acid. The silicon dioxide formed in the event of silicate being present in the soap, is then left undissolved on treatment of the residue with water. Or a known weight of soap may be charred, and the ash supersaturated with hydrochloric acid and thoroughly dried, so that on treatment with water silica and carbon are left undissolved, the latter being ultimately burnt off.

Starch, China Clay, Steatite, Pigments, etc.—Substances of this description other than colouring matters are not often found in soaps, but are occasionally added, especially to certain varieties of fancy soap—*e.g.*, "oatmeal" soap, certain so-called "milk" soaps, and the like. The residue from the previous examination for silicate and carbonate, etc., left undissolved on treating the matters insoluble in alcohol with water consists of these substances. Ultramarine, chrome green, vermilion and similar pigments are detected by the appropriate tests suggested by the colour; starchy matters by means of iodine; mineral constituents generally by incineration; and so on.

The presence of such substances as oatmeal, farina, etc., sometimes renders it necessary slightly to modify the method for determining fatty acids above described, where the cake of fatty acids obtained is weighed, as it may contain some of these matters mechanically intermixed. To separate them the cake is dissolved in ether, benzene, etc., and filtered, the residue well washed, and the filtrate evaporated to dryness.

Glycerol and Sugar.—When glycerol is present (as in the case of soft soaps, cold process soaps, hydrated soaps, etc.) it may be determined, with a fair degree of accuracy, in a variety of ways in the absence of sugar; but in presence of sugar its accurate determination is not easy.

If sugar be not present, one of the simplest methods is to decompose the soap with a slight excess of *sulphuric* acid, and after separating the fatty acids to render the liquid neutral or slightly alkaline with sodium carbonate, evaporate to dryness, and dissolve out the glycerol from the sodium sulphate, etc., by absolute alcohol. The residue left on evaporating off the alcohol may be weighed, and any inorganic matters present determined by incineration and subtracted.

The crude glycerol may, preferably, be purified as described on p. 894; or it may be converted into acetin by acetic anhydride (pp. 893, 898); or if sufficiently free from other organic substances it may be determined by the dichromate process (pp. 888, 901), or oxidised to oxalate (p. 891). A little glycerol is volatilised during the latter part of the evaporation; hence when either of these two latter methods is employed, instead of evaporating the aqueous solution to complete dryness, it may preferably be only partially concentrated.

Muter's method consists in treating the solution with copper sulphate and sodium hydroxide, and determining copper kept in solution colorimetrically or by means of potassium cyanide, parallel observations being made with liquids treated in just the same way after addition of known quantities of glycerol solution from a burette, so as to afford the means of calculating the glycerol present from the amount of copper kept in solution. In general the glycerol may be thus estimated conveniently in the aqueous fluid left after determining total alkali and fatty acids (*supra*).

Sugar, when present, is inverted by heating the solution with dilute hydrochloric or sulphuric acid. The liquid is then rendered alkaline, copper sulphate added in excess, and the sugar calculated from the amount of precipitated cuprous oxide. The alkaline liquid containing glycerol and the products of the oxidation of the sugar may be tested for glycerol by determining the amount of dissolved copper as before, and checking the results by means of similar tests with liquids containing known quantities of sugar + glycerol. The results, however, are apt to be only approximate even with the greatest care. Instead of determining sugar by the copper reduction process the polariscope may be employed. The amount of sugar present and the specific gravity being known, the proportion of glycerol present may be approximately calculated in the case of a liquid containing no other substances in solution.

In *Freyer's* method,[1] based on this principle, a solution of 16 to 28 grammes in 50 to 100 c.c. of water is treated with a solution of barium

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[1] *Chem. Centralbl.*, 1900, i., 693.

chloride until there is no more frothing. The liquid is then diluted to 260 c.c., 10 c.c. being allowed for the precipitate, and the filtrate polarised before and after inversion.

Volatile Substances other than Water.—Sometimes a transparent soap contains alcohol, the proportion of which is desired to be known. Other volatile constituents are sometimes present in other kinds of soap—*e.g.*, carbolic acid, thymol, camphor, etc. In such cases special methods, varying with the nature of the volatile substance, must usually be employed.

Alcohol, if present in quantities above inconsiderable traces, may be determined by dissolving in water a sufficient quantity of soap, adding salt, filtering off, say, one-half of the total fluid, and distilling until about half has passed over. The distillate is similarly redistilled, and ultimately the quantity of alcohol inferred either from the specific gravity of the final distillate, or by oxidation with chromic acid, etc.

The following method of determining *phenoloids* is recommended by Allen[1]:—5 grammes of soap are dissolved in hot water, 20 to 30 c.c. of a 10 per cent. solution of sodium hydroxide added, and the whole cooled and agitated with ether to dissolve hydrocarbons. On separating the alkaline liquid and treating it with strong brine in excess, fatty acid soaps are precipitated, whilst sodium phenolate and cresylate, etc., remain in solution. The liquid is filtered, the precipitate washed with brine, and the filtrate and washings diluted to a litre. 100 c.c. of the solution (representing 0·5 gramme of soap) are acidulated with sulphuric acid, and the solution (clear if fatty acids have been thoroughly removed) titrated with bromine water standardised by means of carbolic acid (or cresylic, etc.), operating in the same way. When enough bromine has been added to cause all the phenoloids to become converted into tribromo derivatives, the yellow tint due to excess of bromine becomes visible. By treating the other 900 c.c. of solution with sulphuric acid and excess of bromine, and shaking it with successive small quantities of carbon bisulphide, the tribromo derivatives may be dissolved out and examined after evaporation of the solvent. Pure phenol (crystallised "carbolic acid") gives nearly colourless long needles of tribromophenol, whereas cresylic acids give deep yellow, orange, or red products, which are either non-crystalline or only crystallise with difficulty; so that the character of the phenoloids present may be ascertained, as well as the amount.

Alder Wright's Scheme of Analysis.—The following general scheme represents a selection from the above processes, which is applicable in most cases:—

Dry 10 grammes *of average sample*, finally at 120° C., and reckon the loss of weight as *water*.

Exhaust the residue with light petroleum spirit, and examine the extract for *unsaponified glycerides, hydrocarbons, spermaceti, wax, cholesterol*, etc.

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[1] *Commercial Organic Analysis*, 2nd edition, ii., 255.

Treat the exhausted residue with water and excess of standard (nitric) acid; separate and weigh the *fatty acids*, and subject them to such further examination as may be required, more especially as regards the presence of *rosin* acids. Titrate the excess of acid in the aqueous liquid so as to determine the *total alkali*, using alkaline solution free from sulphate and chloride. Determine *sulphate* and *chloride* in the neutralised liquid; also *glycerol* and *sugar* if present; and *potassium* if required.

Treat 5 grammes *of average sample* with hot strong alcohol, and titrate acidity or alkalinity of filtered solution. Dissolve the undissolved part in water and titrate for carbonated alkali, etc., so as ultimately to obtain the amount of *free alkali*. Examine the substances not dissolved by alcohol for *silica*, *clay*, *starch*, *pigments*, and similar substances.[1] If unsaponified glycerides and caustic alkali be simultaneously present, the latter should be carbonated before dissolving the soap in alcohol, otherwise a deficiency in the total " free alkali " will result (*supra*, p. 859).

An objection to this mode of operation is that if any caustic alkali be contained in the soap, it becomes more or less carbonated during the drying, so that an incorrect valuation of caustic alkali results. When much caustic alkali is present, it may be determined by the " salting-out " test (*supra*), barium chloride being added to convert alkali carbonate into chloride, and the liquid filtered before titrating (compare p. 859).

Instead of decomposing the soap dissolved in alcohol with excess of standard acid, and titrating with alkali after separation of fatty acids, the alcoholic solution may be rendered neutral to phenol-phthalein, and then directly titrated with a standard mineral acid solution, methyl orange being used as an indicator, since organic fatty acids have no reaction on this substance. Perfectly sharp results are thus obtainable (*Allen*).

Cailletet's Method of Analysis.[2]—For determinations where speed is indispensable but minute accuracy unnecessary, a convenient process has been devised by *Cailletet* for the determination of fatty acids and alkali. A tube holding 50 c.c. and divided into 100 parts is provided, into which are introduced 10 c.c. of diluted sulphuric acid of known strength (about four times normal), 20 c.c. of oil of turpentine, and 10 grammes of the soap in shavings. The tube is closed with a stopper or cork, and well shaken. When all the soap is decomposed the

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[1] Instead of weighing out two portions of soap, one portion (preferably of 10 grammes) may be employed for all the determinations, being first dried, then exhausted with petroleum ether to extract fat, and then treated (still in the Soxhlet tube) with alcohol to dissolve out soap, glycerol, etc. The alcoholic extract thus obtained is titrated for acidity or alkalinity, then largely diluted with hot water and decomposed with standard acid so as to obtain fatty acids and total alkali; while the residue undissolved by alcohol is tested for alkali, silicate, sulphate, chloride, starch, pigments, etc.

[2] *Bull. Soc. Ind.*, Mulhouse, xxix., 8.

tube is allowed to stand, and the volume of the turpentine solution of fatty acids read off.

Subtracting the 20 c.c. of turpentine used, the difference gives the volume of the fatty acids. Thus, if the turpentine solution occupied 50 divisions = 25 c.c., the fatty acids would represent 25 — 20 = 5 c.c. per 10 grammes of soap. Assuming the specific gravity of the fatty acids to be n, their weight would be $5 \times n$ grammes $= 50 \times n$ per cent. by weight. The alkali is obtainable by titrating the excess of the acid.

Cailletet gives the following values for n, experimentally determined by noting the increase in volume of turpentine oil as above indicated, and directly determining the percentage by weight of fatty acids in another portion of the same soap :—

	Specific Gravity of Fatty Acids.
Olive oil (Marseilles) soap,	0·9188
Coconut oil soap,	0·9400
Palm oil soap,	0·9220
Tallow soap,	0·9714
Oleic acid soap,	0·9003

In the case of rosin soaps, the rosin acids do not readily dissolve in the turpentine, 20 c.c. only increasing by 0·15 c.c. in volume by virtue of the rosin acids dissolved, whilst a bulky layer of undissolved rosin collects below the turpentine.

Calcium Salt Test.—A rough method of arriving at the value of a given soap is to dissolve it in dilute alcohol and determine the quantity of the solution that must be added to a known volume of a solution of calcium chloride, sulphate, etc., so as to produce a permanent lather, as in Clark's test for the hardness of water. A parallel determination being made with a standard sample of similar soap of known composition, the ratio between the volumes of the two soap solutions used gives approximately their relative detergent value.

The soap solutions may be conveniently made of the strength of 10 grammes per litre ; whilst the lime salt solution may be prepared by dissolving 0·2 gramme of pure calcium carbonate in dilute hydrochloric acid, evaporating the liquid to dryness on the water-bath to expel excess of acid, dissolving the residue in distilled water, and diluting the liquid to a litre. The solution consequently represents 20 milligrammes of $CaCO_3$ per 100 c.c. or 14 grains per gallon (14° of hardness on Clark's scale).

Representative Analyses.—The following analyses represent the composition of a considerable variety of British and colonial manufacturers' and other scouring and laundry soaps. Where no analyst's name is mentioned, the analyses were made by the author (*A. W.*) :—

	Best Tallow Curd, London make.	Bleached Palm Oil, London make.	Marine Soap, Non-silicated.	Marine Soap, Silicated.	Imitation Castile Soap, English.
Fatty anhydrides, . .	66·60	66·20	32·00	13·50	61·45
Combined alkali (Na_2O), .	7·51	7·83	5·20	2·27	8·46
Free alkali (including that present as silicate), .	0·50	0·40	2·25	8·36	1·16
Silica (SiO_2), . . .	...	...	...	10·50	...
Sodium chloride, . .	1·35	2·05	7·65	5·05	1·17
,, sulphate, . .	0·20	traces	1·45	0·35	1·23
Water, carbonic acid, and insoluble matters, pigments, &c., . . .	23·84	23·52	51·45	59·97	26·53 [1]
	100·00	100·00	100·00	100·00	100·00
Percentage of true soap, .	74·11	74·03	37·20	15·77	69·91
Mean molecular weight of fatty acids, . . .	284	271	200	197	234

	"Primrose," London make.	"Ivory," Canadian.[1]	"Cold Water," English.	"Cold Water," Canadian.[2]	Oleic Acid Soap, London make.
Fatty anhydrides, . .	46·88	43·33	43·70	45 85	62·71
Resinous anhydrides, . .	15·40	25·00	22·00	24·00	...
Combined alkali (Na_2O), .	7·12	7·72	9·28	8·00	7·36
Sodium carbonate, . .	0·14	2·64	0·58	2·22	0·68
,, chloride, . .	0·14	21·31	24·44	19·93	29·25
,, sulphate, . .	0·07				
Water with minute quantities of insoluble matters, lime, ferric oxide, &c., .	30·25				
	100·00	100·00	100·00	100·00	100·00
Percentage of true soap, .	69·40	76·05	74·98	72·07	70·07
Free alkali (Na O), . .	0·08	1·54	0·34	1·30	0·40
Mean molecular weight of fatty acids, &c., . .	280	283	230	280	273

[1] Including 0·74 per cent. of insoluble pigments.

[2] Exhibited in the "Colonial and Indian Exhibition," London, 1886. For analyses of various of the Colonial soaps, made by the author, *vide* "Colonial and Indian Exhibition Reports—Oils and Fats" (*Leopold Field*).

Manufacturers' Soaps (C. Hope).

	"Cold Water" Soap, Tallow, Rosin, and Cotton-seed Oil.	"Marseilles No. 1," chiefly Olive Oil.	"Palm Oil No. 1."	"Mottled" Palm-kernel Oil, Cold Process.	"Marine," for Use of Emigrants: Palm-kernel Oil, Cold Process.	"Pale Rosin," Tallow, and Rosin.
Fatty anhydrides and rosin, .	71·30	62·66	59·28	38·89	19·42	60·90
Soda (Na_2O), combined as soap,	7·98	7·27	6·65	5·76	3·11	7·22
Free alkali (Na_2O), including carbonate and silicate,	1·23	0·80	0·40	2·91	6·98	0·10
Sodium chloride, . . .	0·36	0·76	0·47	1·78	5·13	0·46
,, sulphate, . . .	0·30	0·30	0·13	0·72	0·35	0·12
Silica, ...	1·07	0·06	0·42	6·40	9·00	0·04
Lime, oxide of iron, &c., .	0·16	0·16	0·16	0·03	0·16	0·02
Water, ...	17·44	28·20	32·35	38·70	53·32	31·22
Total, ...	99·84	100·21	99·86	95·19[1]	97·47[1]	100·08
Actual soap present, . .	79·28	69·93	65·93	44·65	22·53	68·12

Manufacturers' Soaps (Lant Carpenter).

	"Primrose" Soap.		"Cold Water" Soap.	"Neutral Curd."	"Oil" Soap, "Oleic Acid."
	Genuine Rosin Soap (South of England).	Watered & Silicated (North of England).			
Fatty acids,[2] . . .	62·3	42·66	70·2	67·9	68·6
Combined soda (Na_2O), .	6·7	5·41	7·3	7·0	7·88
"Free alkali" (Na_2O), .	...	1·21	1·8	nil.	1·0
Silica, ...	...	0·94	1·6	...	...
Neutral salts, . . .	0·2	0·55	0·4	0·2	1·0
Water, ...	32·8	50·40	22·0	28·0	21·0
Total, . . .	102·0	101·17	103·3	103·1	99·48

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[1] Glycerol present, but not determined.

[2] Not calculated to fatty anhydrides.

Pharmaceutical Soaps (*M. Dechan*).

	Sapo durus, Hard Soap.	*S. Castil. albus*, White Castile.	Mottled Castile.	*S. Animalis*, Tallow Soap.	*S. Mollis*, Soft Soap.
Fatty acids,[1] . .	81·50	76·70	68·10	78·30	48·50
Combined alkali, . . .	9·92	9·14	8·90	9·57	12·60
Free alkali, ...	0·08	0·09	0·19	0·28	0·30
Silica, ...	...	...	0·15	...	0·17
Sulphates and chlorides, .	0·28	0·36	0·63	0·47	0·93
Matters insoluble in alcohol,	0·50	0·60	1·30	1·10	1·60
Other insoluble matter, .	0·20	0·90	0·80	0·40	1·00
Water, ...	10·65	13·25	21·70	12·50	39·50
	103·13	101·04	101·77	102·62	104·68

Soft Soaps (*Ure*).

	London Soft Soap.	Belgian Green Soap.	Scotch.	Rape Oil Soft Soap.	Olive Oil Soft Soap.
Fatty acids, ...	45·0	36·0	47·0	51·7	48·0
Dry potassium oxide (K_2O), .	8·5	7·0	8·0	10·0	10·0
Water, salts, glycerol, &c., .	46·5	57·0	45·0	38·3	42·0
	100·0	100·0	100·0	100·0	100·0

In general, similar partial analyses of soft soaps meet the objects in view, inasmuch as such soaps are generally purchased in quantity under contract either to yield a given percentage (40, 50, etc.) of fatty acids on decomposition by a mineral acid, or to lose not more than a given percentage in weight (water) on drying completely. The degree of alkalinity is usually judged by the "touch" or taste of the sample, the tongue being regarded as a sufficiently delicate indicator for such purposes. When more definite information is required the methods above described are applicable. Thus the water is directly determined by drying on a sand-bath (p. 855); the total fatty acids, free alkali, combined alkali, unsaponified oil, and matters insoluble in water (such as starch added to simulate "figging," etc.) by the respective processes above detailed; the rosin acids by Gladding's process (p. 862) or Twitchell's or Fortini's methods (p. 864); silicate by incineration and analysis of the mineral constituents of the ash; and so on.[1]

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[1] *The Bureau of Standards, Dept. of Commerce*, U.S.A. Circular No. 62, Dec. 16, 1916, has fixed standards for the permissible limits of water, volatile matter, alkali, sodium chloride, etc., in different commercial kinds of soap (see *J. Soc. Chem. Ind.*, 1917, xxxvi., 392).

Household Soaps.—In the case of household and laundry soaps it is to be noticed that the physical consistence of the substance is in many cases of as much importance as its chemical constitution. From the consumer's point of view, what is required in the case of a hard soda soap is an article from which, during use, no more is dissolved or abraded than is just requisite for the object in view. If the soap be of too soft a consistency (either through over-watering, or bad selection of materials), a much larger amount is rubbed on the clothes, etc., to be washed or scoured than is absolutely necessary, leading to much waste. On the other hand, pure tallow curd soaps largely boiled down are so hard as only to rub off and lather with difficulty. With manufacturers' soaps intended to be dissolved in water before use (*e.g.*, soft soap for wool-scouring, etc.), the rate of solution must be sufficient for the purpose; whilst hydrocarbons and other insoluble impurities which might spot and stain goods must be absent from soaps intended for treatment during dyeing and subsequent operations.

Toilet Soaps.

	High-class Milled Soap of Continental make.	High-class Opaque Soap, English.	Inferior Opaque Soap, English.	Transparent Soaps Made by		
				Cold Process.	Spirit Process.	
				Sugared.		Genuine, not Sugared.
Fatty anhydrides,	83·60	60·20	65·00	38·90	65·60	68·10
Uncombined rosin and unsaponified fats,	1·00	...	...	0·40	3·00	3·20
Combined alkali,	9·80	6·98	8·91	5·57	7·73	7·62
Sodium carbonate,	0·24	0·17	1·73	3·80	nil.	0·20
Sugar,	...	...	...	28·00	14·00	nil.
Glycerol,	...	3·00	6·00	3·00	...	7·00
Water and minute quantities of salts,	5·36	29·65	18·36	20·33	9·67	13·88
	100·00	100·00	100·00	100·00	100·00	100·00
Percentage of true soap,	93·40	67·18	73·91	44·47	73·33	75·72
Free alkali (Na_2O),	0·14	0·10	1·01	2·22	nil.	nil.
Mean molecular weight of fatty acids,	274	276	226	225	272	286

Toilet Soaps.—In the case of "toilet" soaps, the most important quality is that of furnishing a sufficient lather without at the same time causing the application of too alkaline a substance to the skin. The small amount of free alkali developed by hydrolysis when a tablet of soap is rubbed on the skin or between the hands is practically insensible, excepting to extremely sensitively skinned persons, who, in consequence, are rarely able to use soap in any form without suffering from more or less irritating effects. Such individuals are comparatively rare; but a much larger portion of the population, especially ladies and young children, are prone to suffer inconvenience (particularly in windy and wintry weather) through the use of soap containing more than traces of free alkali. To some extent this inconvenience may be mitigated by introducing into the soap such substances as vaseline, spermaceti, or even purified lard, etc., whereby a film of greasy or unguent-like substance is left adherent to the skin, or at least pressed into its pores (*vide* p. 839); but a far safer plan is so to prepare or refine the soap as to ensure that it shall not contain any material amount of free alkali. The author (*A. W.*) has proposed[1] to classify toilet soaps into three grades from this point of view, viz.:—

First Grade.—Soaps containing a total amount of "free alkali" not exceeding $\frac{1}{40}$ (2·5 per 100) of the alkali present combined with fatty anhydrides as soap; so if the soap contained 8·0 per cent. of combined alkali, the free alkali would not exceed 0·2 per cent.

Second Grade.—Soaps in which the "free alkali" ranges between $\frac{1}{40}$ and $\frac{3}{40}$ (2·5 to 7·5 per 100) of that present as actual soap—*i.e.*, for a soap containing 8·0 per cent. of combined alkali the free alkali would be between 0·2 and 0·6 per cent.

Third Grade.—Soaps in which the "free alkali" exceeds $\frac{3}{40}$ (7·5 per 100) of that present as actual soap.

It is to be borne in mind, however, that other possible ingredients besides alkali are apt to be detrimental to sensitive skins. Of these *sugar* (at one time almost invariably present in transparent soaps) is the one most certainly known to be noxious (pp. 840, 842, 843); but there is also reason for supposing that some extremely highly perfumed soaps may exert a more or less marked irritating action of the same kind in virtue of the comparatively high proportion of essential oils, etc., present (p. 840), even though entirely destitute of free alkali, and containing no sugar.

When a soap (toilet, household, or manufacturer's) contains an amount of glycerol approximately corresponding with that equivalent to the fatty acids found (92 parts glycerol) for $3 \times n$ parts of fatty acids of mean molecular weight n), the probability is that the soap has been prepared by a cold process; such a soap, for instance, might yield fatty acids of mean molecular weight 270, in which case 100 parts of fatty acids would correspond with $\frac{92 \times 100}{3 \times 270} = 11{\cdot}3$ parts of glycerol, if triglycerides were employed. Larger proportions of glycerol can only be contained in cases where extra glycerol has been added. On the other hand, as soaps prepared by boiling and "salting out" contain no glycerol at all, the presence of smaller proportions of glycerol suggest either that the soap mass is a mixture of hydrated soaps or cold process soaps (p. 818) and boiled soaps, or that free oleic acid, etc., has been employed along with glycerides in its manufacture.

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[1] "Cantor Lectures," Society of Arts (*J. Soc. Arts*, 1885, xxxiii., 1124), where also various other analyses of toilet soaps are given.

CHAPTER XXIII.

GLYCEROL EXTRACTION—MANUFACTURE OF GLYCERIN.

In the manufacture of soaps and "stearine" for candle-making, large quantities of glycerol[1] are produced as a product complementary to the fatty acids liberated by saponification of the oils and fats employed. Until comparatively recently, much of the glycerol thus formed was wasted, being run away with other watery fluids into the drains, etc.; but since the introduction of various applications for which glycerol is suited, more especially the manufacture of dynamite and other explosives, much of the substance formerly thrown away as worthless, is now extracted and utilised by processes which substantially consist of evaporation so as to remove saline matters by crystallisation, and distillation of the final mother liquors with superheated steam.

Methods of Separating Glycerol.—The "sweet water" obtained in the saponification of glycerides by lime in the autoclave or open pan processes (pp. 717, 724), is one of the most suitable sources of commercial glycerin when required of high purity. The distillation of fatty matters by means of superheated steam, so as to hydrolyse them and form fatty acids and glycerol (p. 742), furnishes a still purer raw product; though if the temperature of distillation be too high (above 310° to 320° C.), more or less decomposition of glycerol into water and acrolein (acrylic aldehyde) results.

The aqueous glycerol solutions thus obtained are concentrated by evaporation, preferably not in ordinary pans, but by special devices analogous to those used in the sugar industry, where a series of convoluted tubes or hollow plates heated by the internal admission of steam is made to revolve, so that the tubes or plates partly dip into the fluid to be evaporated and carry upwards an adherent film thereof as they revolve. This film rapidly loses water by evaporation, whilst the part of the tube or plate to which it adheres is exposed to the air after emerging from the liquid, especially if the whole arrangement is placed inside an exhausted vessel or "vacuum pan."

When the glycerol solution is sufficiently concentrated, it is decolorised by treatment with animal charcoal, and again distilled by means of superheated steam,[2] the processes being repeated several times

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[1] As already stated the word "glycerol" is employed in the present work to denote the chemical substance $C_3H_5(OH)_3$, and the term "glycerin" to indicate commercial products consisting more or less largely of glycerol in varying states of purity.

[2] An improved form of glycerin rectifying apparatus was patented by R. O. Unglaub (Eng. Pat. 8,196, 1889).

for products of high purity, such as the glycerin required for the manufacture of nitro-glycerin for dynamite and similar explosives. Glycerins of the highest degree of purity are best obtained by crystallising, draining off the unsolidified portion by a centrifugal machine, and melting the residual crystals.

The extraction and purification of glycerol from soap lyes is a much more troublesome matter, not so much because of the dissolved salt, etc., which requires to be removed as the evaporation proceeds, as because various organic impurities derived from the fats, etc., are also present. *Kingzett*[1] found the composition of the salts deposited on evaporation, and of the evaporated mother liquor of specific gravity 1·236 to be as follows :—

SALTS.

Sodium chloride,	78·12
Sodium sulphate,	8·61
Sodium carbonate,	2·61
Insoluble organic matter,	0·22
Glycerol and other organic soluble substances,	3·55
Water,	7·50
	100·61

CRUDE GLYCERIN.

	Pounds per gallon.
Water,	7·53
Glycerol,	2·04
Salts,	2·78
	12·35

At the present day crude glycerins show a much greater degree of purity than this.

The removal of the inorganic salts and the saponaceous, resinous, and albuminous organic matters contained in the crude lyes may be more or less completely effected in a variety of ways, the subject of a number of patents. Thus, by acidifying the liquor any soap is decomposed, whilst fatty and resinous acids are set free, and can be separated by filtration. By treatment with carbon dioxide any caustic alkali is carbonated, and its removal by salting out on evaporation rendered more easy (*Versmann*). By adding tannin in some form or other, albuminous matters may be coagulated and precipitated (*Payne*). The substitution of sodium sulphate for common salt in the "salting-out" process is said to facilitate the separation of saline matters on evaporation, whilst the residual sodium sulphate interferes less with the purification by distillation, ultimately necessary to render the glycerol suitable for most of the purposes for which it is employed (*Benno, Jappé & Co.*).

Hill (Eng. Pat. 17,860, 1894) recommends the use of caustic soda or of a mixture of caustic soda and sodium carbonate instead of salt

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[1] *J. Soc. Chem. Ind.*, 1882, i., 77.

for "salting out." The lye is then used to saponify more fat, and a concentration of glycerol effected.

Spent lyes produced when black ash liquors are directly used for soap-making, contain a variety of impurities not present when purer caustic soda is used, especially that made by the ammonia process. Such liquors may be considerably purified by the addition of soluble copper salts, whereby thiocyanates and organic matters, etc., are precipitated (*Allen* and *Nickels*); or they may be neutralised and oxidised with calcium hypochlorite.

Droux and *Depoully* have devised a method of obtaining pure glycerol solutions, which consists in heating the residue, left on evaporation of the lyes, with oleic acid at 170° to 175° C. in an atmosphere of carbon dioxide. The glyceride formed by the combination of the oleic acid with the glycerol is then washed with water, and the glycerol liberated.

A few years ago the *Michaud Frères process* for saponifying glycerides with zinc oxide (p. 731) instead of lime attracted considerable attention, it being expected that fatty acids and glycerol would be so readily obtained that the older soap boiling processes would be superseded, and direct neutralisation processes (p. 812) substituted for them, whilst almost pure glycerol would result, as in the candle-making lime autoclave process.

According to *Jean*[1] the process, now known as *Poulain* and *Michaud's* process, gives a 6 per cent. glycerin on heating 3,000 kilos. of oil with 10 kilos. of zinc dust for six hours under a pressure of 8 to 9 kilos. per square centimetre. This process, however, is not in general use.

A similar remark applies to methods based on saponification with ammonia solution under pressure.

In France glycerin is to a large extent obtained by the hydrolysis of stearine with water and magnesia under pressure, which is said to give better yields and a purer product than treatment with 3 per cent. of lime under a smaller pressure (*Jean*).

Liberation of Fatty Acids and Glycerol by means of Sulpho-Fatty Acids.—In *Twitchell's* process (Eng. Pat. 4,741, 1898) the neutral fats, to which are added a small quantity of free fatty acids, are treated with about 1 per cent. of a sulpho-derivative of a fatty acid, such as sulpho-stearic acid, etc., and boiled after the addition of 50 per cent. of water. At the end of the operation the sulpho-reagent is recovered by precipitation with sulphuric acid, or a metallic salt such as lime. Claim is made in the same patent for the "sulpho-fatty aromatic compounds" described above, which, owing to their great stability, are said to be capable of extended use in the arts (see also p. 736).

Van Ruymbeke's Process.—One form of apparatus used in the treatment of soap lyes is shown in Fig. 177. The waste lye from the settling tanks is nearly neutralised with sulphuric or hydrochloric acid, if necessary, in the treating tank A, which contains steam pipes

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[1] *J. Soc. Chem. Ind.*, 1896, xiv., 282.

and an air jet, and is then treated with the calculated quantity of a solution of basic ferric sulphate. This precipitates fatty acids in the form of iron soaps, which are separated by forcing the lye by means of the pump B through the filter-press C. After further purification in a

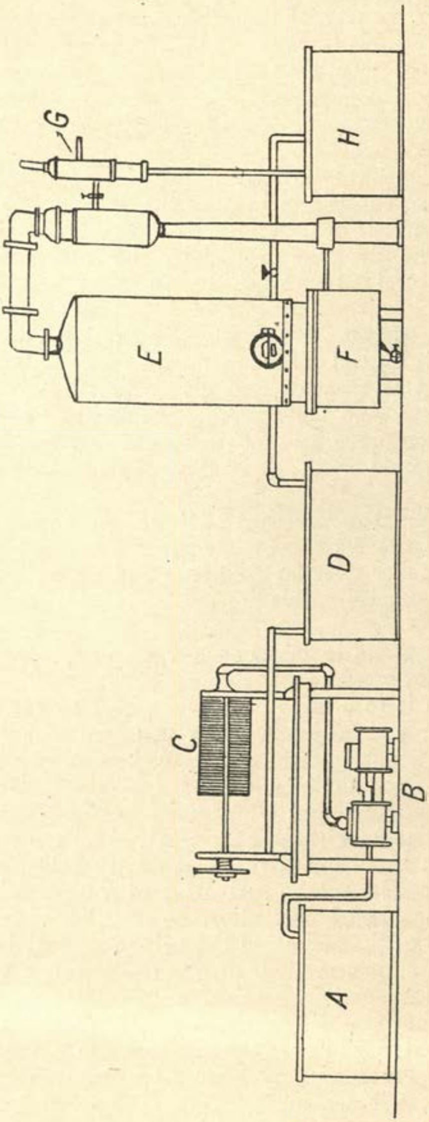

Fig. 177.—Van Ruymbeke's Process of Glycerol Recovery from Soap Lye.

A. Treating tank.
B. Pump.
C. Filter press.
D. Storage tank.
E. Steam jacketed evaporator.
F. Salt filter.
G. Ejector vacuum pump.
H. Receiver.

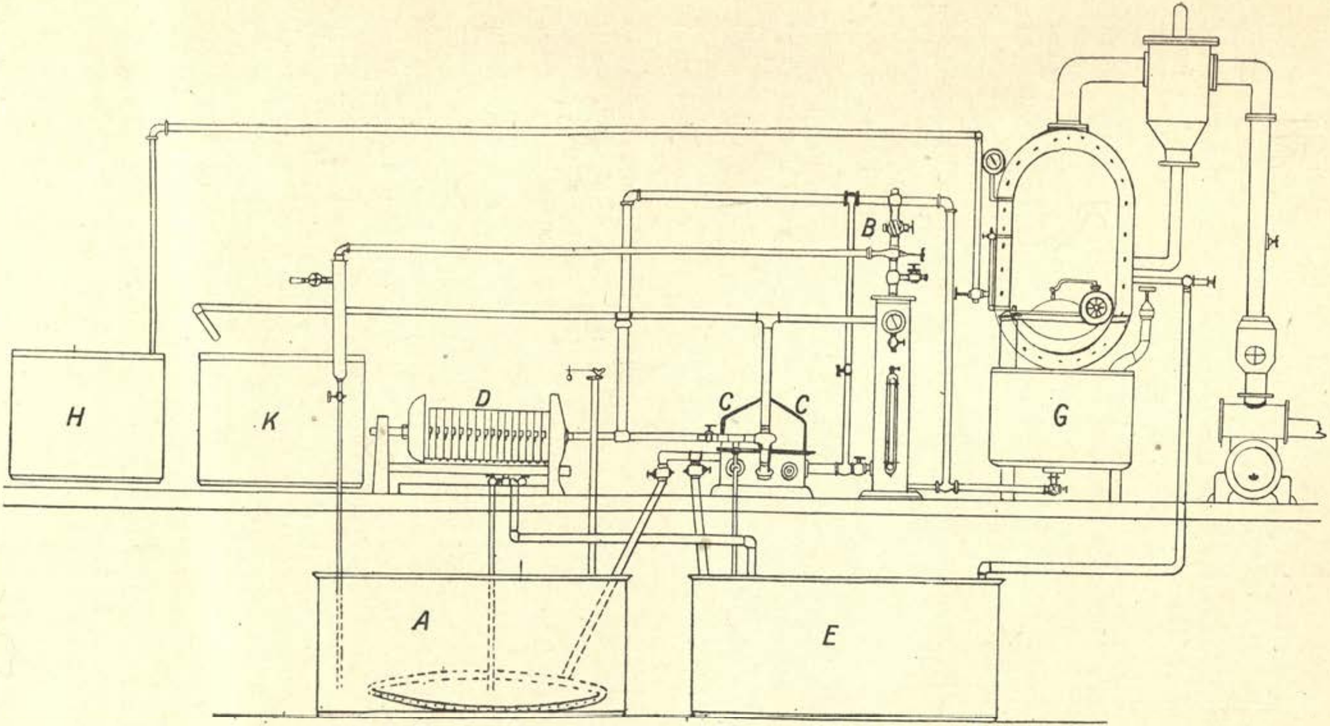

Fig. 178.—Garrigue's Process for Glycerol Recovery from Waste Soap Lye.

A. Treating tank.
B. Körting exhauster.
C. Pump.
D. Filter press.
E. Feeding tank.
F. Vacuum evaporator.
G. Salt filter.
H. Settling tank.
K. Receiver.

similar tank, the filtration is repeated, and the clear acid filtrate is then agitated in the tank D with the calculated amount of soda ash to neutralise it, and is subsequently concentrated in one or more evaporators E connected with the vacuum pump G. Most of the dissolved salt will have separated when the solution has been concentrated to 50 per cent. of glycerol. The liquid is then withdrawn, filtered from the deposit, and transferred to a smaller evaporator, where the concentration is continued until about 80 per cent. of glycerol is present.

Garrigue's Process of Recovery.—Fig. 178 represents Garrigue's plant, which is extensively used in the recovery of glycerol. The waste soap lyes are run from a storage tank into the tank A, where they are treated with about 0·5 per cent. of alum or aluminium sulphate, and sufficient sulphuric acid to render the liquid nearly neutral.

After the mixture has been thoroughly agitated by means of air blown into it from the Körting exhauster B, it is forced by means of the pump C through the filter-press D into the tank E, and thence to the vacuum evaporator F, where it is concentrated until the liquid contains about 40 per cent. of glycerol, and about 80 per cent. of the salts have crystallised from it.

It is next passed through the salt filter G into the settling tank H, where it is agitated with about 0·5 per cent. of barium chloride. This precipitates the residual sodium sulphate and any soap still remaining, and sufficient sulphuric acid is now added to decompose the alkali compounds of soluble fatty acids, which then combine with the barium and are largely precipitated together with the excess of barium chloride.

The liquid is once more passed through D into E and F, and again concentrated until it contains about 85 per cent. of glycerol, and is finally pumped into the receiver K, where it is treated with the calculated quantity of sodium carbonate (soda ash) to render it slightly alkaline, and is then ready for distillation.

Fermentation Glycerin.—The glycerin water separated in the enzymic process of hydrolysing glycerides (p. 739) is a fairly pure source of glycerol. It is technically known as "fermentation glycerol."

Electrolytic Production.—In a process patented by *Glatz* and *Lugo* (Eng. Pat. 10,837, 1896) the soap lye is subjected to the action of an electric current; the anode being composed of zinc on carbon in contact with the lye, whilst the cathode is separated by a porous partition. The liberated sodium is attracted to the cathode, and immediately oxidised to sodium hydroxide. The glycerol is liberated, whilst albuminoid and colouring matters are rendered insoluble, the colour of the lye changing from dark brown to light straw colour. After the separation of the insoluble matter the liquid is distilled, yielding pure colourless glycerin. The caustic soda solution is at once available for a further saponification.

Jobbin's Distillation Plant.—The crude glycerol, as obtained by one of the processes described, is purified by distillation, the plant represented in Fig. 179 being one which is frequently employed.

The still A is made of steel, and is heated by means of a closed coil, through which is conducted a current of dry steam at 150° C., while free dry steam is also introduced through the jet *b b*. Simultaneously a vacuum is maintained within the vessel.

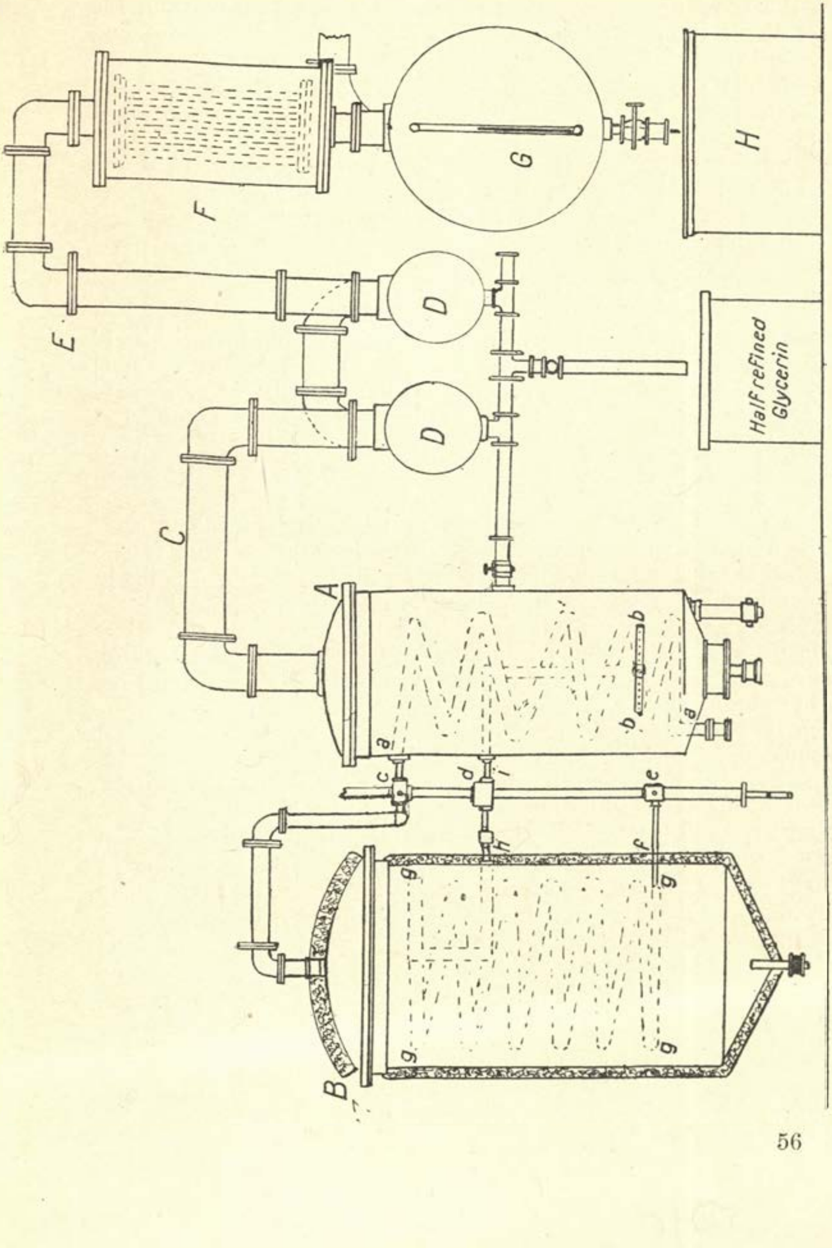

Fig. 179.—Jobbin's Glycerol Distilling Apparatus.

A. Steel boiler (still).
B. Steam-heated chamber, felt-covered.
a a. Closed steam coil.
b b. Open jet for current of live steam.
c. Entry for steam.
c d e. Passage of steam.
e f. Tube for expansion of steam.
g g g. Wide steam coil.
h i. Passage for dry steam from B to A.
C. Pipe.
D. Drums.
E. Pipe.
F. Cooler.
G. Sweet water drum.
H. Sweet water tank.

The temperature of the steam expanding from the tube *ef* into the wider coil *ggg* is lowered, but is again raised to 150° C. by the free steam in the superheating chamber B. Thence the steam is forced through *hi* into the still A and issues from the jet *bb* into the glycerol. Under the combined action of the dry steam and the vaccum, the glycerol distils through C into the drums D D, while the steam and more volatile constituents of the lye are condensed in the cooler F, and drawn off into the tank H. During the distillation the level of the liquid in the still is kept constant by the admission of fresh supplies of crude glycerol.

The "sweet water" in H, and the half-refined glycerin in H are purified by further distillation, whilst the glycerol (about 30 to 50 per cent.) contained in the residue of "glycerol foots" in the still is recovered by special treatment.

Examination of Glycerin.

Impurities.—Commerical glycerins often contain impurities of various descriptions best estimated by direct determination. Lime, lead, magnesia, saline matters, and similar non-volatile substances are left behind on evaporation and incineration, and may be examined in the ordinary ways.

Distilled glycerins only contain minute amounts of inorganic matter, rarely exceeding 0·1 to 0·2 per cent.

Silver nitrate forms no precipitate or darkening in colour after standing 24 hours when added to glycerins free from acrolein, formic acid, or other substances capable of reducing silver salts, but the liquid shows considerable discoloration when such substances are present.[1]

Traces of chlorides are not precipitated by silver nitrate, silver chloride being slightly soluble in glycerol. Glycerins from soap lyes, however, give copious precipitates, as they usually contain several per cents. of sodium chloride.

Such lyes often contain *resinous matters*, *proteins*, *fatty acids*, and other substances precipitable by basic lead acetate.

Cane sugar and *glucose* are sometimes used to adulterate glycerin. They are readily detected by means of Fehling's solution.

Trimethylene Glycol.—An abnormally light glycerin examined by *Noyes* and *Watkins*[2] yielded, on distillation, a liquid boiling at 214° to 217° C., and having a specific gravity of 1·056 at $\frac{20^\circ}{15^\circ}$ C. They concluded that this substance, identified as trimethylene glycol, was formed by spontaneous saponification and fermentation of the glycerol in the fat before being used in the soap factory. Its presence would be dangerous in glycerin intended for the manufacture of nitroglycerin, since it reacts explosively with nitric acid. It is indicated by the low

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[1] According to *Ritsert*, pure glycerol gives neither deposit of metallic silver, nor formation of yellow colour when mixed with its own volume of ammonia solution, heated to boiling, and treated with silver nitrate.

[2] *J. Amer. Chem. Soc.*, 1895, xvii., 890.

specific gravity of the glycerin, and a high result in the dichromate method of determining the glycerol (*infra*).

Dynamite Glycerin.—Glycerin intended for the manufacture of nitroglycerin must show a considerable degree of purity, and in particular be free from, or contain only slight traces of, certain substances that might interfere with the nitration, or with the stability of the nitrated product.

The following details are based upon the methods of analysis published by *Barton*[1] and by *Lewkowitsch*.[2]

Specific Gravity.—This is most readily determined by means of the Sprengel tube. A good dynamite glycerin usually has a specific gravity of about 1·262 to 1·264 at 15·5° C. It should not be less than 1·261 (*Lewkowitsch*).

Permanent Specific Gravity.—This is the name given by *Barton* to the specific gravity of glycerin that has been heated at 225° to 230° C., so as to expel volatile hydrocarbons, etc. In a good sample it is about 1·2653 (*Barton*).

Carbonaceous Residue and Ash.—Barton heats from 4·5 to 5·5 grammes of the glycerin in a porcelain crucible, until ignition occurs, and then leaves the mass to burn out, and weighs the carbonaceous residue. In the case of a good glycerin he found it to amount to about 0·012 per cent. The residue is then further ignited over a low Argand flame until all carbon has burned off, and the white residue weighed. There should be only a trace of ash, and it should be free from calcium (and magnesium and aluminium, *Lewkowitsch*).

Chlorine.—This should not be present in more than slight traces. *Barton* neutralises 100 c.c. of the glycerin with sodium carbonate, and titrates the liquid with deci-normal silver nitrate. In his opinion a good glycerin should not contain more than about 0·002 per cent.

Arsenic.—On diluting 10 c.c. of the glycerin with 20 c.c. of water, acidifying the liquid with hydrochloric acid, introducing a bright strip of copper, and heating the flask on the water-bath for about twenty minutes, the copper should not show more than a slight stain of arsenic (Reinsch's test).

Lewkowitsch's test is to mix 1 c.c. of the glycerin with 2 c.c. of water, render the liquid just alkaline with ammonia, and add a few drops of a solution of silver nitrate, when there should be no yellow turbidity produced.

Organic Impurities.—The silver nitrate test described above is applied, but less rigorously than in the case of pharmaceutical glycerin.

Lewkowitsch considers the glycerin sufficiently pure if no reduction occurs, within ten minutes, on mixing 3 c.c. of the diluted glycerin (1 : 2), with a few drops of a 10 per cent. solution of silver nitrate.

Total Residue.—According to *Lewkowitsch* the residue left on drying the glycerin slowly, at a temperature of 160° C., should not exceed 0·15 per cent.

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[1] *Ibid.*, 1885, xvii., 277.

[2] *J. Soc. Chem. Ind.*, 1895, xiv.

Acidity.—Dynamite glycerin should contain not more than traces of free acid. *Barton* dilutes 100 c.c. of the sample with twice that amount of water, boils the liquid with 10 c.c. of normal alkali, and titrates the excess of the latter with normal hydrochloric acid, using phenol-phthalein as indicator.

Higher Fatty Acids.—On passing nitrous vapours through the diluted glycerin warmed on the water-bath, for about two hours, and subsequently still further diluting the liquid, there should be no flocculent deposit (formation of elaidic acid).

Neutrality.—Fifty c.c. of glycerin diluted with 100 c.c. of water should not require more than 0·3 c.c. of normal acid or alkali for neutralisation (*Barton*).

Nitration Test.—A practical test of the suitability of a glycerin for the manufacture of nitroglycerin is to nitrate a small quantity of the sample, and observe its behaviour.

The acid employed for the nitration is prepared by mixing 1 part of nitric acid of specific gravity, 1·5 with 2 parts of sulphuric acid of specific gravity, 1·845, and cooling the mixture. The use of the sulphuric acid is to act as a dehydrating agent during the nitration. This mixture can be prepared long before it is required, and kept in a stoppered bottle.

In the nitration test 10·5 grammes of the glycerin are weighed out into a small beaker, whilst 47 c.c. of the acid mixture are placed in another beaker holding about 200 c.c. This second beaker, in which is also placed a thermometer, is held firmly in the right hand, with the thermometer passing between the fingers, and partially immersed below the surface of water contained in a large basin, so that the level of acid within the beaker is about the same as that of the water on the outside.

The glycerin is then allowed to fall drop by drop into the beaker, which is meanwhile continuously moved about with a circular motion in the basin of water, so as thoroughly to mix the contents, and at the same time keep them cool.

The utmost care is necessary to prevent any water splashing into the beaker, the result of which would be a sudden rise of temperature, and possible explosion. Throughout the operation the temperature should not exceed about 25° C., and if any signs of a sudden rise (above 30° C.) are observed, or if red fumes appear, the beaker should be instantly broken by means of the thermometer, so as to plunge the contents into the large volume of water in the basin.

When the nitration is complete the contents of the beaker are transferred to a graduated 100 c.c. cylinder, with a side tap, and allowed to stand for the nitroglycerin layer to separate.

The separation should take place within a few minutes, and the nitroglycerin should form a sharply-defined layer at the top, and be free from flocculent matter in suspension.

An approximately quantitative idea of the yield is shown by the number of c.c. occupied by the layer in the cylinder.

In order to dispose of the nitroglycerin the acid layer is drawn off through the side tap of the cylinder, and the nitroglycerin poured into a large beaker of water, washed once or twice by decantation, and finally taken up with kieselguhr, and the dynamite quietly burned.

Lewkowitsch (*loc. cit.*) uses larger quantities of glycerin and nitration acids, 50 grammes of the glycerin being introduced into 375 grammes of the acid mixture, contained in a 500 c.c. beaker, which is partially immersed in a current of cold water, passing through a vessel, the same precautions being taken as described above.

A rough quantitative determination is obtained by separating the nitroglycerin from the acid, washing it in a funnel with water at 35° to 40° C., then with a 20 per cent. solution of sodium hydroxide, and again with water, and its volume measured in a 100 c.c. burette. The number of c.c. multiplied by 1·6 gives approximately the weight in grammes. The yield is usually 207 to 210 per cent., whilst the theoretical quantity is 246·7 per cent.

Detection of Glycerol.—For the qualitative detection of glycerol in aqueous solutions a variety of tests have been proposed, one of which (Reichl's) is described on p. 7. *Kohn*[1] recommends the following method:—The liquid to be examined is evaporated with potassium bisulphate and the residue heated in a retort; if glycerol is present, acrolein is formed, so that the distillate gives a red coloration on treatment with a solution of rosaniline that has been just decolorised by sulphurous acid.

Quantitative Determination of Glycerol.—Numerous processes have been devised for the quantitative determination of glycerol, some of which are only suitable under particular conditions. Thus in the case of distilled glycerins of considerable or tolerable purity where organic matters are absent and inorganic constituents and water are the only impurities (no glucose or other sugar, etc., being present as adulterations), the amount of glycerol may be conveniently ascertained by oxidation with potassium bichromate and sulphuric acid (*vide infra*).

Another method applicable under such conditions is the "acetin process" of Benedikt (*vide infra*).

Two readily applied physical methods are applicable in the case of glycerol solutions which contain no appreciable amount of interfering impurity, so that practically only glycerol and water are present. These are based respectively on the determination of the specific gravity at 15° C., and of the refractive index at the same temperature.

Calculation of Glycerol from the Specific Gravity and Refractive Index.—*Skalweit* gives the following table[2] for the purpose of examining glycerol solutions in these ways. Older tables have also been published by *Strohmer*[3] and by *Lenz*,[4] reproduced by *Benedikt*.[5]

Hehner[6] considers Lenz's table accurate, and *Richmond* has recalculated it to 15·5° C.

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[1] *J. Soc. Chem. Ind.*, 1890, ix., 148.

[2] *Repert. anal. Chem.*, v., 18.

[3] *Monat. für Chem.*, v., 61.

[4] *Zeit. anal. Chem.*, xix., 302.

[5] *Analyse der Fette*, 2nd Ed., 256, *et seq*

[6] *J. Soc. Chem. Ind.*, 1889, viii., 4.

Specific Gravity at 15·5° (*Lenz, recalculated by Richmond*).

Percentage of Glycerol.	Specific Gravity at 15·5°.	Percentage of Glycerol.	Specific Gravity at 15·5°.
100	1·2674	87	1·2327
99	1·2647	86	1·2301
98	1·2620	85	1·2274
97	1·2594	84	1·2248
96	1·2567	83	1·2222
95	1·2540	82	1·2196
94	1·2513	81	1·2169
93	1·2486	80	1·2143
92	1·2460	79	1·2117
91	1·2433	78	1·2090
90	1·2406	77	1·2064
89	1·2380	76	1·2037
88	1·2353	75	1·2011

According to *Grün* and *Wirth*,[1] anhydrous glycerol has the specific gravity of 1·2653 ± 0·0001, a value which is in agreement with that of *Gerlach*.[2]

Specific Gravity and Refractive Index of Glycerol Solutions (*Skalweit*).

Percentage of Glycerol.	Specific Gravity at 15° C.	Refractive Index for D at 15° C.	Percentage of Glycerol.	Specific Gravity at 15° C.	Refractive Index for D at 15° C.
100	1·2650	1·4742	50	1·1290	1·3993
98	1·2600	1·4712	48	1·1236	1·3966
96	1·2550	1·4684	46	1·1182	1·3938
94	1·2499	1·4655	44	1·1128	1·3910
92	1·2447	1·4625	42	1·1074	1·3882
90	1·2395	1·4595	40	1·1020	1·3854
88	1·2341	1·4565	38	1·0966	1·3827
86	1·2287	1·4535	36	1·0912	1·3799
84	1·2233	1·4505	34	1·0858	1·3771
82	1·2179	1·4475	32	1·0804	1·3743
80	1·2125	1·4444	30	1·0750	1·3715
78	1·2071	1·4414	28	1·0698	1·3687
76	1·2017	1·4384	26	1·0646	1·3660
74	1·1963	1·4354	24	1·0594	1·3633
72	1·1909	1·4324	22	1·0542	1·3607
70	1·1855	1·4295	20	1·0490	1·3581
68	1·1799	1·4265	18	1·0440	1·3555
66	1·1743	1·4235	16	1·0390	1·3529
64	1·1686	1·4205	14	1·0340	1·3503
62	1·1628	1·4175	12	1·0290	1·3477
60	1·1570	1·4144	10	1·0240	1·3452
58	1·1514	1·4104	8	1·0192	1·3426
56	1·1458	1·4084	6	1·0144	1·3402
54	1·1402	1·4054	4	1·0096	1·3378
52	1·1346	1·4024	2	1·0048	1·3354

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[1] *Zeit. angew. Chem.*, 1919, xxxii., 59.

[2] *Chem. Ind.*, vii., 277.

David recommends the following process for determining the amount of glycerol formed on saponification:—100 grammes of fat are heated with 65 of crystallised barium hydroxide, and 80 c.c. of 95 per cent. alcohol added with agitation. The nearly solid mass is boiled with 500 c.c. of water and allowed to settle; the residue left on pouring off the supernatant fluid is washed twice by decantation, and the total

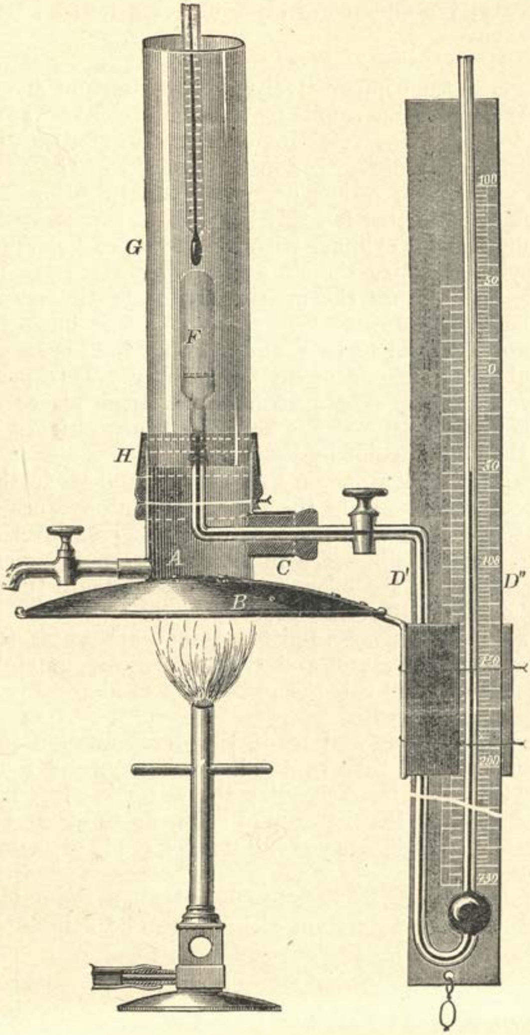

Fig. 180.—Gerlach's Vaporimeter.

fluid evaporated to half its bulk with sulphuric acid, the surplus being removed by barium carbonate. Finally the filtered fluid is evaporated to 50 c.c. and examined either as to its refractive power or as to its specific gravity, the amount of glycerol being found by means of the table given above.

Gerlach's Vaporimeter.—Another physical process is also available for such fluids as the comparatively pure solutions of glycerol obtained in the course of preparing candle materials (autoclave " sweet waters "), or for distilled glycerins retaining only small quantities of impurities. This is based on the differences in the tension of the vapour emitted by glycerol solutions of various degrees of concentration.

Gerlach's vaporimeter for this purpose is represented in fig. 180. A B is a hollow metal cylinder with a cup-shaped bottom for heating; G a glass cylinder fitting therein and made water-tight by the india-rubber ring, H. To use the instrument, G is disconnected and the whole turned upside down. The reservoir, F, is filled with mercury and a little of the fluid to be examined, and then connected by a bit of rubber tubing to the end of the pressure tube, D D, passing inwards through the tube, C. The instrument is then placed upright and filled with hot water after G has been fixed in position, and the water brought to the boiling point by heating B.

The expansion of the mercury on heating and its further expulsion by the vapour emitted from the glycerol solution cause the pressure tube, D D, to be filled with mercury up to a given level. The length in millimetres of the difference in level between the mercury in the reservoir and that in the open limb of the pressure tube (known by means of the attached scales) represents the difference between the tension of aqueous vapour admitted from pure water (equal to the existing barometric pressure) and that of the vapour emitted by the glycerol solution. From this the percentage of glycerol is reckoned by means of the table opposite.

Grün and *Wirth* (*loc. cit.*) made the determination in a capillary tube extension to a T tube containing mercury, and found that the method could be used for estimating the water in glycerin, the results not being affected by the presence of salts, up to about 1 per cent. of sodium chloride. But it was not suitable for crude glycerins containing polyglycerols.

Dichromate Methods.—These are based upon the oxidation of the glycerol by means of potassium dichromate and sulphuric acid, as in the equation—

$$3C_3H_8O_3+7K_2Cr_2O_7+28H_2SO_4=7K_2SO_4+7Cr_2(SO_4)_3+40H_2O+9CO_2,$$

and the calculation of its amount from the proportion of oxygen consumed, or from the amount of carbon dioxide evolved.

Hehner's Method.[1]—For this the following solutions are required:—(i.) Potassium dichromate solution containing 74·86 grammes of dichromate and 150 c.c. of sulphuric acid per litre. This is standardised on

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[1] *J. Soc. Chem. Ind.*, 1889, viii., 6.

Percentage of Glycerol.	Specific Gravity of Solution.		Boiling Point of Solution.	Tension of Vapour emitted at 100° C.	Diminution in Tension Compared with Water giving 760 Millimetres.
	At 15° C. Water at 15° C. = 1.	At 20° C. Water at 20° C. = 1.			
			Degrees C.		
100	1·2653	1·2620	290	64	696
99	1·2628	1·2594	239	87	673
98	1·2602	1·2568	208	107	653
97	1·2577	1·2542	188	126	634
96	1·2522	1·2516	175	144	616
95	1·2526	1·2490	164	162	598
94	1·2501	1·2464	156	180	580
93	1·2476	1·2438	150	198	562
92	1·2451	1·2412	145	215	545
91	1·2425	1·2386	141	231	529
90	1·2400	1·2360	138	247	513
89	1·2373	1·2333	135	263	497
88	1·2346	1·2306	132·5	279	481
87	1·2319	1·2279	130·5	295	465
86	1·2292	1·2252	129	311	449
85	1·2265	1·2225	127·5	326	434
84	1·2238	1·2198	126	340	420
83	1·2211	1·2171	124·5	355	405
82	1·2184	1·2144	123	370	390
81	1·2157	1·2117	122	384	376
80	1·2130	1·2090	121	396	364
79	1·2102	1·2063	120	408	352
78	1·2074	1·2036	119·0	419	341
77	1·2046	1·2009	118·2	430	330
76	1·2018	1·1982	117·4	440	320
75	1·1990	1·1955	116·7	450	310
74	1·1962	1·1928	116	460	300
73	1·1934	1·1901	115·4	470	290
72	1·1906	1·1874	114·8	480	280
71	1·1878	1·1847	114·2	489	271
70	1·1850	1·1820	113·6	496	264
65	1·1710	1·1685	111·3	533	227
60	1·1570	1·1550	109	565	195
55	1·1430	1·1415	107·5	593	167
50	1·1290	1·1280	106	618	142
45	1·1155	1·1145	105	639	121
40	1·1020	1·1010	104	657	103
35	1·0885	1·0875	103·4	675	85
30	1·0750	1·0740	102·8	690	70
25	1·0620	1·0610	102·3	704	56
20	1·0490	1·0480	101·8	717	43
10	1·0245	1·0235	100·9	740	20
0	1·0000	1·0000	100·0	760	0

iron ammonium sulphate or metallic iron. (ii.) Ferrous ammonium sulphate solution (240 grammes per litre). This is equivalent to the dichromate solution. (iii.) A more dilute solution of the dichromate solution (1 : 10).

For the determination of the amount of glycerol in fats, about 3 grammes are saponified with alcoholic potassium hydroxide, the soap solution diluted to 200 c.c., the fatty acids liberated by the addition of dilute sulphuric acid, and the filtrate concentrated to half its volume, so as to completely remove all alcohol.

It is then mixed with 25 c.c. of sulphuric acid and 50 c.c. of the strong dichromate solution, and the covered beaker heated in a boiling water-bath for two hours, after which the liquid is titrated with the ferrous ammonium solution, which is added in slight excess, and the excess titrated with the weaker dichromate solution, potassium ferricyanide being used as indicator. One c.c. of the dichromate solution consumed corresponds with 0·01 gramme of glycerol. Operating in this way *Hehner* obtained the following percentages of glycerol:—

Olive oil,	10·26 per cent.
Cod-liver oil,	9·87 ,,
Linseed oil,	10·24 ,,
Margarine,	10·01 ,,
Butter fat,	11·96 to 12·4 ,,

Obviously, if any traces of alcohol are left in the fluid, or if soluble acids or other organic matters capable of reducing dichromate are present, the results will be too high.

When chlorides of aldehydic compounds are present (*e.g.*, acrolein in distilled glycerins), the slightly diluted glycerol solution is first warmed in a flask with silver oxide. Basic lead acetate is then added in slight excess, the fluid made up to a definite volume and filtered, and an aliquot part treated with dichromate solution as described above.

Richardson and *Jaffé*[1] have described a simpler modification of Hehner's process, in which the glycerol solution is heated for twenty minutes only with the dichromate, and only one dichromate solution is required.

In their modification, 25 grammes of the glycerin are diluted with the same quantity of water, 25 c.c. of the solution treated with 7 c.c. of the pharmacopœial solution of basic lead acetate, and the precipitate repeatedly washed with cold water. The filtrate and washings (about 150 c.c.) are treated with sulphuric acid to precipitate the excess of lead, and the liquid made up to 250 c.c. and filtered. Twenty c.c. of the filtrate are placed in a beaker (the opening of which is covered by a funnel with a short stem), and mixed, first with 25 c.c. of Hehner's dichromate solution, and then with 25 c.c. of strong sulphuric acid.

The beaker is then placed in the hot water-bath for twenty minutes, after which the liquid is cooled, diluted to 250 c.c., and titrated upon 20 c.c. of a solution containing 2·982 per cent. of ferrous ammonium sulphate, potassium ferricyanide being used as indicator.

The amount of iron solution taken representing 0·01 gramme of glycerol, the required percentage of glycerol, x, is obtained by the following formula—

$$x = (0{\cdot}25 - \frac{250}{A} \times 0{\cdot}01) \times 500$$

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[1] *Ibid.*, 1898, xvii., 330.

where A represents the number of c.c. of dichromate mixture required, and 0·25 is the equivalent of glycerol represented by the 25 c.c. of the dichromate solution taken.

In the case of spent lyes 2·5 grammes are diluted to 50 c.c., the chlorides and organic impurities precipitated by means of basic lead acetate, the lead sulphate filtered off, the filtrate concentrated to about 25 c.c., and the glycerol determined as described above.

Gailhat[1] finds that in the methods of Hehner and of Richardson and Jaffé the oxidation with dichromate is incomplete unless the vapours first evolved (formic acid, formaldehyde, etc.), are condensed and brought into action again. If, however, the reaction be carried out by boiling the liquid for at least fifteen minutes under a reflux condenser, this loss of primary oxidation products is prevented.

Measurement of the Liberated Carbon Dioxide.—Legler's method, in which the oxidation is carried out in a weighed carbonic acid apparatus and the amount of carbon dioxide estimated by the loss in weight, is obviously not very reliable.

A direct measurement of the carbon dioxide, however, as recommended by *Cross* and *Bevan*, and more recently by *Gantter*,[2] is much more satisfactory. The reaction is carried out in a flask connected with a gas-measuring apparatus, and the gas measured in the usual way and calculated to the standard temperature and pressure. One c.c. of carbon dioxide corresponds with 1·296 milligrammes of glycerol.

Permanganate Methods.—In the absence of organic substances capable of forming oxalic acid under the influence of alkaline permanganate, moderately sharp valuations may be obtained by converting the glycerol into oxalate (*Wanklyn* and *Fox; Benedikt* and *Zsigmondy; A. H. Allen*). The liquid is rendered strongly alkaline and boiled with excess of permanganate; this is destroyed by sodium sulphite or sulphur dioxide and the liquid filtered and the oxalic acid precipitated as calcium oxalate.

The oxidation that occurs may be represented by the equation—

$$C_3H_8O_3 + 3O_2 = C_2H_2O_4 + CO_2 + 3H_2O.$$

When this process is applied to the determination of the amount of glycerol furnished on saponification by a given oil or fat, the preliminary saponification should be effected by means of potassium hydroxide and pure methylic alcohol. The solution obtained by saponifying 2 to 3 grammes of oil is evaporated, and the residue treated with hot water and hydrochloric acid. The liberated fatty acids (the solidification of which on cooling may be accelerated by the addition of a little paraffin wax) are filtered off and washed, and the filtrate neutralised and then treated with 10 grammes of potassium hydroxide. A 5 per cent. solution of potassium permanganate (or the powdered salt) is next added in sufficient quantity to render the liquid blue or blackish; after which the whole is heated to the boiling point,

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[1] *Mon. Scient.*, 1902, xvi., 89; *J. Soc. Chem. Ind.*, 1902, xxi., 280.

[2] *Zeit. anal. Chem.*, 1895, xxxiv., 421.

whereby hydrated manganese dioxide separates, and the fluid becomes red. Aqueous solution of sulphur dioxide is now introduced until complete decolorisation is effected. The liquid is then filtered, the filtrate acidified with acetic acid (whereby any turbidity due to passage of manganese dioxide through the filter is removed by the action of the sulphurous acid set free), and the oxalic acid present precipitated by calcium chloride or acetate. The calcium oxalate is ignited, dissolved in excess of semi-normal acid and titrated back with semi-normal alkali, methyl orange being used as indicator. One c.c. of *normal* acid (2 c.c. of semi-normal) corresponds with 46 milligrammes of glycerol.

The quantity of glycerol thus found is close to, but generally a little below, that calculated from the saponification equivalent of the substance on the assumption that only triglycerides are present.[1] In the case of oxidised drying oils, however, a notable excess is observed, doubtless on account of the formation of other products yielding oxalic acid by oxidation. Thus *Benedikt* and *Zsigmondy* obtained the following values :—

Name of Oil, &c.	Glycerol calculated from the Saponification Equivalent.	Glycerol found by Oxalic Acid Process.
Olive oil, ...	10·49 to 11·10	10·15 to 10·38
Coconut oil, . . .	14·76 to 14·83	13·3 to 14·5
Tallow, ...	10·72	9·94 to 10·21
Cow's butter fat, . . .	12·51	11·59
Linseed oil, ...	10·24 to 10·66	9·45 to 9·97
Skins from boiled linseed oil,	...	15·5 (*Allen*)

The table opposite gives the amounts of glycerol theoretically obtainable from 100 parts of the triglycerides of the respective acids named; the last column indicating the amount of fatty acid simultaneously produced.

In the case of the higher acids the sum of the glycerol and fatty acids is approximately constant—viz., 106 to 107 per 100 of glyceride used.

Mangold's Method.—*Mangold*[2] modifies the oxalic acid process by dissolving 0·4 gramme of the glycerin to be tested in 300 c.c. of water containing 10 grammes of potassium hydroxide, and introducing a 5 per

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[1] If E is the mean saponification equivalent of a mixture of triglycerides, 3 E milligrammes of the mixture theoretically yield 92 of glycerol

$$= \frac{92}{3\,E} \times 100, \text{ or } \frac{3{,}065{\cdot}7}{E} \text{ per cent.}$$

[2] *Zeit. angew. Chem.*, 1891, 400.

Glyceride of	Formula of Acid.	Percentage of Glycerol.	Percentage of Fatty Acid.
Butyric acid, . . .	$C_4H_8O_2$	30·5	87·41
Lauric ,, . . .	$C_{12}H_{24}O_2$	14·4	94·04
Myristic ,, . . .	$C_{14}H_{28}O_2$	12·7	94·47
Palmitic ,, . . .	$C_{16}H_{32}O_2$	11·42	95·28
Stearic ,, . . .	$C_{18}H_{36}O_2$	10·34	95·73
Oleic ,, . . .	$C_{18}H_{34}O_2$	10·41	95·70
Ricinoleic ,, . . .	$C_{18}H_{34}O_3$	9·98	95·92
Linolic ,, . . .	$C_{18}H_{32}O_2$	10·48	95·67

cent. solution of potassium permanganate until it amounts to 1·5 times the theoretical amount (1 of glycerol = 6·87 of potassium permanganate). After standing half an hour hydrogen peroxide solution is added until all the manganese is precipitated. A known fraction of the total fluid is filtered off, boiled for half an hour to destroy excess of hydrogen peroxide, acidified with sulphuric acid after cooling, and titrated with standard permanganate solution so as to determine the oxalic acid produced.

Hehner and *Mitchell* have found that the amount of permanganate specified above is insufficient, and that half as much again is essential for the complete oxidation of the glycerol.

An objection to the permanganate process, which does not apply to the dichromate methods, is that lower fatty acids (butyric acid, etc.) are also oxidised to oxalic acid, so that inaccurate results are obtained with crude glycerides or spent lyes from coconut or palm-kernel oil soaps.

Oxidation in Acid Solution.—Planchon, and more recently *Gailhat* (*loc. cit.*), devised methods of oxidising the glycerol in a strongly acid, instead of an alkaline, solution.

Acetin Process.[1]—This is based upon the conversion of the glycerol into triacetin, when heated with an excess of acetic anhydride and anhydrous sodium acetate, and the determination of the amount of potassium hydroxide neutralised by the acetic acid formed on saponification of the triacetin (after removal of the excess of acetic anhydride by boiling the liquid with water).

In this reaction 92 parts of glycerol correspond with 3 × 56·1 = 168·3 parts of potassium hydroxide thus neutralised.

In carrying out this process from 1 to 1·5 grammes of the glycerin is boiled with about 3 grammes of anhydrous sodium acetate and 7 to 8 grammes of acetic anhydride for 1 to $1\frac{1}{2}$ hours under a reflux condenser. The liquid is then cooled, diluted with 50 c.c. of water, and

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[1] Benedikt and Cantor, *Zeit. angew. Chem.*, 1888, 460.

again heated under a reflux condenser, until solution is complete. It is next filtered, and the filtrate cooled and exactly neutralised with dilute sodium hydroxide solution. Twenty-five c.c. of a standardised (10 per cent.) solution of sodium hydroxide are then introduced by means of a pipette, the liquid boiled for 15 minutes, and the excess of alkali titrated as rapidly as possible with normal hydrochloric acid, 1 c.c. of which corresponds with 0·03067 gramme of glycerol.

Richardson and *Jaffé* (*loc. cit.*) consider that this process, although giving very accurate results, requires too much attention to detail for ordinary laboratory purposes. (*Cf.*, however, p. 898 *infra.*)

Glycerol in Soap Lyes.—On account of the organic impurities and large amounts of inorganic salts present in soap lyes, the above methods are not, as a rule, directly available for the estimation of glycerol in such liquors. By evaporation these may be concentrated without material loss of glycerol at first, although subsequently a perceptible amount is carried away with the escaping water vapour as the liquors become highly concentrated. When the evaporation is carried nearly to dryness a residue is obtained from which nearly absolute alcohol dissolves out glycerol together with more or less inorganic matter.

A rough estimate of the glycerol present may be obtained by evaporating the alcoholic solution to dryness and weighing the residue, which is then gently incinerated so as to burn off organic matter, the weight of ash left being deducted from that of the total residue. If, however, other organic matters soluble in alcohol be present, obviously they would thus be reckoned as glycerol.

In some cases a partial purification of the glycerol may be brought about by again evaporating the alcoholic extract, treating the residue with a small quantity of absolute alcohol, and then adding one and a-half times the volume of ether; glycerol is kept in solution, but some of the other organic matters are usually precipitated, so that a partial purification is brought about.

In other cases the crude glycerol may be purified by treatment with neutral or basic lead acetate to precipitate colouring matters, etc.

When rosin is present the liquors may be conveniently purified by evaporation after neutralisation with dilute sulphuric acid and the addition of a little milk of lime (whereby most of the rosin is converted into insoluble calcium salts) and filtration. The residue is treated with a mixture of three volumes of absolute alcohol and one of pure ether, the dissolved matter weighed (after evaporation of the solvent) and corrected for ash left on incineration (*Fleming*).

Muter's Process.[1]—Another process consists of heating the crude glycerol liquors with basic lead acetate to remove certain kinds of organic matters that would interfere with the subsequent part of the test, filtering, removing the lead by hydrogen sulphide, and then treating the liquid with sodium or potassium hydroxide, and dropping in copper sulphate solution with continuous agitation until copper hydroxide remains permanently undissolved. The quantity of copper

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[1] *Analyst*, 1881, vi., 41.

contained in the blue solution is about proportionate to the amount of glycerol present (under certain conditions—*vide infra*), so that by determining the dissolved copper the glycerol is known.

For this purpose *Muter* employs a standard solution of potassium cyanide, for which the author (*A. W.*) substituted a colorimetric process based on comparison of the hue of the tinted fluid (filtered) with that of a known relative thickness of copper solution containing a known amount of copper also dissolved in glycerol solution under the same conditions.[1]

Unless the proportion of caustic alkali present is uniform, a measurable difference in the solvent power of glycerol for copper hydroxide is noticeable, as the amount of alkali varies (*Puls*); so that when a cyanide solution is used it should be standardised by means of a known glycerol copper solution prepared in exactly the same way, and tested under the same conditions as the substance under examination.

Acetin and Oxidation Processes.—Crude glycerol solution, purified by basic lead acetate, usually retains but little (if any) organic matters of an alcoholiform or hydroxylated character, so that the acetin method (*supra*) can generally be applied without serious error to the residue left on evaporation and extraction with alcohol. This, however, is not so certainly the case as regards the oxalate method, there being a possibility of obtaining oxalate by the oxidation of organic matters other than glycerol; whilst in the author's opinion, the dichromate process is usually inapplicable, organic impurities being generally still left which readily reduce dichromate.

Richardson and *Jaffé*, however, state that good results are obtained by their modified process (*vide supra*).

Lead Oxide Method.—A method sometimes employed is to heat a quantity of crude glycerin, representing about 2 grammes of glycerol, with 40 grammes of litharge to about 130° C., taking care that no carbon dioxide has access to the mass. When the weight becomes constant the whole is similarly heated to 160° C., at which temperature the glycerol is volatilised excepting that a molecule of water remains behind combined with the lead oxide, so that the loss of weight is $\frac{74}{92}$ times the glycerol present. Hence the loss of weight at 160° C.

International Standard Methods (1911).[2]—The valuation of crude glycerol has in recent years assumed greater commercial importance owing to the increased value of the commodity. The want of uniformity in the methods and processes of analyses, together with the irregularity of the results obtained, emphasised the desirability for the standardisation of crude glycerol analysis; so, with this object in view, committees were formed in America, France, Germany, and Great Britain. These committees worked, in the first instance, independently, but were

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[1] Alder Wright, "Cantor Lectures," *J. Soc. Arts*, 1885, xxxiii., 1123.

[2] *Analyst*, 1911, xxxvi., 314-321.

ultimately brought together and after a series of conferences the conclusions arrived at by the various committees were summarised and drawn up in the form in which they are now presented. The methods detailed in this report have the unanimous support of each of the above committees, and are strongly recommended by them as International Standards.

Sampling.—The most satisfactory method available for sampling crude glycerol liable to contain suspended matter, or which is liable to deposit salt on settling, is to have the glycerol sampled by a mutually approved sampler as soon as possible after it is filled into drums, but in any case before any separation of salts has taken place. In such cases he shall sample with a sectional sampler (a suitable sampling apparatus is described in an appendix to the report), then seal the drums, brand them with a number for identification, and keep a record of the brand number. The presence of any visible salt or other suspended matter is to be noted by the sampler, and a report of same made in his certificate, together with the temperature of the glycerol. Each drum must be sampled. Glycerol which has deposited salt or other matters cannot be accurately sampled from the drums, but an approximate sample can be obtained by means of the sectional sampler, which will allow a complete vertical section of the glycerol to be taken, including any deposit.

Analysis.—1. *Determination of Free Caustic Alkali.*—Weigh 20 grms. of the sample into a 100 c.c. flask, dilute with approximately 50 c.c. of freshly-boiled distilled water, add an excess of neutral barium chloride solution, 1 c.c. of phenol-phthalein solution, make up to the mark, and mix. Allow the precipitate to settle, draw off 50 c.c. of the clear liquid, and titrate with normal acid ($\frac{N}{1}$). Calculate to percentage of Na_2O existing as caustic alkali.

2. *Determination of Ash and Total Alkalinity.*—Weigh 2 to 5 grms. of the sample in a platinum dish, burn off the glycerol over a luminous Argand burner or other source of heat giving a low flame temperature, the temperature being kept low to avoid volatilisation and the formation of sulphides. When the mass is charred to the point that water will not become coloured by soluble organic matter, lixiviate with hot distilled water, filter, wash, and ignite the residue in the platinum dish. Return the filtrate and washings to the dish, evaporate, and carefully ignite without fusion. Weigh the ash.

Dissolve the ash in distilled water and titrate total alkalinity, using as indicator methyl orange cold or litmus boiling.

3. *Determination of Alkali present as Carbonate.*—Take 10 grms. of the sample, dilute with 50 c.c. distilled water, add sufficient $\frac{N}{1}$ acid to neutralise the total alkali found at (2), boil under a reflux condenser for fifteen to twenty minutes, wash down the condenser tube with distilled water, free from carbon dioxide, and titrate back with $\frac{N}{1}$ NaOH, using phenol-phthalein as indicator. Calculate the percentage of Na_2O. Deduct the Na_2O found in (1). The difference is the percentage of Na_2O existing as carbonate.

4. *Alkali combined with Organic Acids.*—The sum of the percentages of Na_2O found at (1) and (3) deducted from the percentage found at (2) is a measure of the Na_2O or other alkali combined with organic acids.

5. *Determination of Acidity.*—Take 10 grms. of the sample, dilute with 50 c.c. of distilled water free from carbon dioxide, and titrate with $\frac{N}{1}$ NaOH and phenol-phthalein. Express in terms of Na_2O required to neutralise 100 grms.

6. *Determination of Total Residue at* 160° *C.*—For this determination the crude glycerol should be slightly alkaline with Na_2CO_3, not exceeding the equivalent of 0·2 per cent. Na_2O, in order to prevent loss of organic acids. To avoid formation of polyglycerols, this alkalinity must not be exceeded.

Preparation of Glycerol.—Ten grms. of the sample are weighed into a 100 c.c. flask, diluted with water, and the calculated quantity of $\frac{N}{1}$ HCl or Na_2CO_3 added to give the required degree of alkalinity. The flask is filled to 100 c.c., the contents mixed, and 10 c.c. measured into a weighed Petrie or similar dish 2·5 inches diameter and 0 5 inch deep, which should have a flat bottom. In the case of crude glycerols abnormally high in organic residue, a less quantity is to be evaporated, so that the weight of organic residue does not materially exceed 30 to 40 mgrms.

Evaporation of the Glycerol.—The dish is placed on a water-bath (the top of the 150° C. oven acts equally well) until most of the water has evaporated. From this point the evaporation is effected in the oven. Satisfactory results are obtained in an oven measuring 12 inches cube, having an iron plate $\frac{3}{4}$ inch thick lying on the bottom to distribute the heat. Strips of asbestos millboard are placed on a shelf halfway up the oven. On these strips the dish containing the glycerol is placed.

If the temperature of the oven has been adjusted to 160° C. with the door closed, a temperature of 130° to 140° C. can be readily maintained with the door partially open, and the glycerol, or most of it, should be evaporated off at this temperature. When only a slight vapour is seen to come off, the dish is removed and allowed to cool.

An addition of 0·5 to 1 c.c. of water is made, and by a rotatory motion the residue brought wholly or nearly into solution. The dish is then allowed to remain on a water-bath or top of the oven until the excess water has evaporated and the residue is in such a condition that on returning to the oven at 160° C. it will not spit. The time taken up to this point cannot be given definitely, nor is it important. Usually two to three hours are required. From this point, however, the schedule of time must be strictly adhered to. The dish is allowed to remain in the oven, the temperature of which is carefully maintained at 160° C. for one hour, when it is removed, cooled, the residue treated with water, and the water evaporated as before. The residue is then subjected to a second baking of one hour, after which the dish is allowed to cool in a desiccator over sulphuric acid and weighed. The treatment with water, etc., is repeated until a constant loss of 1 to 1·5 mgrms. per hour is obtained.

Corrections to be Applied to the Weight of the Total Residue.—In the case of acid glycerol, a correction must be made for the alkali added. One c.c. $\frac{N}{1}$ alkali represents an addition of 0·022 grm. In the case of alkaline crudes a correction should be made for the acid added. Deduct the increase in weight due to the conversion of the NaOH and Na_2CO_3 to NaCl. The corrected weight, multiplied by 100, gives the percentage of *total residue at* 160° *C.*

Preserve the total residue for the determination of the non-volatile acetylisable impurities.

7. *Organic Residue.*—Subtract the ash from the total residue at 160° C. Report as organic residue at 160° C. (*Note.*—It should be noted that alkaline salts of organic acids are converted to carbonates on ignition, and that the CO_3 radicle thus derived is not included in the organic residue.)

8. *Moisture.*—This test is based on the fact that glycerol can be completely freed from water by allowing it to stand *in vacuo* over sulphuric acid or phosphoric anhydride.

Two to three grms. of very pure bulky asbestos freed from acid-soluble material which has been previously dried in a water-oven are placed in a small stoppered weighing-bottle of about 15 c.c. capacity. The weighing-bottle is kept in a vacuum desiccator furnished with a supply of concentrated sulphuric acid, under a pressure equivalent to 1 to 2 mm. of mercury, until constant in weight. From 1 to 1·5 grm. of the sample is then carefully dropped on the asbestos in such a way that it will be all absorbed. The weight is again taken, and the bottle replaced in the desiccator under 1 to 2 mm. pressure until constant in weight. At 15° C. the weight is constant in about forty-eight hours. At lower temperatures the test is prolonged.

The sulphuric acid in the desiccator must be frequently renewed.

Acetin Process for Glycerol Determination.—This process is the one agreed upon at a Conference of Delegates from the American, British, French, and German Committees, and has been confirmed by each of the above Committees as giving results nearer to the truth on crudes in general, and is the process to be used (if applicable) whenever only one method is employed. On pure glycerols the results are identical with those of the bichromate process. For the application of this process the crude glycerol should not contain over 50 per cent. water.

The following reagents are required :—

1. *Best Acetic Anhydride.*—This should be carefully selected. A good sample must not require more than 0·1 c.c. normal NaOH for saponification of the impurities when a blank is run on 7·5 c.c. Only a slight colour should develop during digestion of the blank.

2. *Pure Fused Sodium Acetate.*—The purchased salt is again completely fused in a platinum, silica, or nickel dish, avoiding charring, powdered quickly, and kept in a stoppered bottle or in a desiccator. It is most important that the sodium acetate be anhydrous.

3. *A Solution of Sodium Hydroxide for Neutralising, of about $\frac{N}{1}$ Strength, Free from Carbonate.*—This can be readily made by dissolving pure sodium hydroxide in its own weight of water (preferably water free from carbon dioxide), and allowing to settle until clear, or filtering through an asbestos or paper filter. The clear solution is diluted with water free from carbon dioxide to the strength required.

4. $\frac{N}{1}$ *Sodium Hydroxide, Free from Carbonate.*—Prepared as above, and carefully standardised.

Some sodium hydroxide solutions show a marked diminution in strength after being boiled ; such solutions should be rejected.

5. $\frac{N}{1}$ *Acid.*—Carefully standardised.

6. *Phenol-phthalein Solution.*—0·5 per cent. phenol-phthalein in alcohol and neutralise.

The Method.—Into a narrow-mouthed flask (preferably round-bottomed), capacity about 120 c.c., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1·25 to 1·5 grms. of the glycerol. Add first about 3 grms. of the anhydrous sodium acetate, then 7·5 c.c. of the acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9 to 10 mm. inside.

The flask is connected to the condenser by either a ground glass joint (preferably) or a rubber stopper. If a rubber stopper is used, it should have had a preliminary treatment with hot acetic anhydride vapour.

Heat the contents and keep just boiling for one hour, taking precautions to prevent the salts drying on the sides of the flask.

Allow the flask to cool somewhat, and through the condenser tube add 50 c.c. of the carbon-dioxide-free distilled water, heated to about 80° C., taking care that the flask is not loosened from the condenser. The object of cooling is to avoid any sudden rush of vapours from the flask on adding the water, and to avoid breaking the flask. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify and the test proceeded with the next day without detriment. The contents of the flask may be warmed to, but must not exceed, 80° C. until the solution is complete, except a few dark flocks representing organic impurities in the crude. By giving the flask a rotatory motion, solution is more quickly effected. Cool the flask and contents without loosening from condenser. When quite cold wash down the inside of the condenser tube, detach the flask, wash off stopper or ground glass connection into the flask, and filter contents of flask through an acid-washed filter into a Jena glass flask of about 1 litre capacity. Wash thoroughly with cold distilled water free from carbon dioxide. Add 2 c.c. of phenol-phthalein solution (F), then run in sodium hydroxide solution (C) or (D) until a faint pinkish-yellow colour appears throughout the solution. This neutralisation must be done most carefully. The alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling with occasional agitation or change of motion until the solution is nearly neutralised, as indicated by the slower disappearance of the colour developed locally by the alkali running into the mixture. When this point is reached the sides of the flask are washed down with carbon-dioxide-free water and the alkali subsequently added drop by drop, mixing after each drop until the desired tint is obtained.

Now run in from a burette 50 c.c. or a calculated excess of $\frac{N}{1}$ NaOH (D), and note carefully the exact amount. Boil gently for fifteen minutes, the flask being fitted with a glass tube acting as a partial condenser; cool as quickly as possible, and titrate excess of NaOH with $\frac{N}{1}$ acid (E) until the pinkish-yellow or chosen end-point colour just remains. A further addition of the indicator at this point will cause a return of the pinkish colour; this must be neglected, and the first end-point taken.

From the $\frac{N}{1}$ NaOH consumed calculate the percentage of glycerol after making the correction for the blank test described below:

1 c.c. of $\frac{N}{1}$ NaOH = 0·03069 grm. of glycerol.

The coefficient of expansion for normal solutions is approximately 0·00033 per c.c. for each degree C. A correction should be made on this account if necessary.

Blank Test.—As the acetic anhydride and sodium acetate may contain impurities which affect the result, it is necessary to make a blank test, using the same quantities of acetic anhydride and sodium acetate as in the analysis. After neutralising the acetic acid, it is not necessary to add more than 5 c.c. of the $\frac{N}{1}$ alkali (D), as that represents the excess of alkali usually left after saponification of the triacetin in the glycerol determination.

Determination of the Glycerol Value of the Acetylisable Impurities.—The total residue at 160° C. is dissolved in 1 or 2 c c. of water, washed into a clean acetylising flask 120 c.c. capacity, and the water evaporated. Now add anhydrous sodium acetate, and proceed as in the glycerol determination before described. Calculate the result to glycerol.

Analysis of Acetic Anhydride.—Into a weighed stoppered vessel, containing 10 to 20 c.c. of water, run about 2 c.c. of the anhydride, replace stopper and weigh; allow to stand, with occasional shaking, for several hours, till all anhydride is hydrolysed; then dilute to about 200 c.c., add phenol-phthalein, and titrate with $\frac{N}{1}$ NaOH. This gives the total acidity due to free acetic acid and acid formed from anhydride.

Into a stoppered weighing-bottle containing a known weight of recently distilled aniline (from 10 to 20 c c.) measure about 2 c.c. of the sample, stopper, mix, allow to cool, and weigh. Wash contents into about 200 c c. cold water, and titrate acidity as before. This yields the acidity due to the original, preformed, acetic acid plus one-half the acid due to anhydride (the other half having formed acetanilide); subtract the second result from the first (both calculated for 100 grms.) and double result, obtaining c.c. $\frac{N}{1}$ NaOH per 100-grm. sample. One c.c. NaOH equals 0·0510 grm. of acetic anhydride.

Dichromate Process for Glycerol Determination. Reagents Required.—(*a*) *Pure Potassium Dichromate* powdered and dried in air free from dust or organic vapours, at 110° to 120° C. This is taken as the standard.

(*b*) *Dilute Dichromate Solution.*—7·4564 grms. of the above dichromate (*a*) are dissolved in distilled water and the solution made up to 1 litre at 15·5° C.

(*c*) *Ferrous Ammonium Sulphate.*—Dissolve 3·7282 grms. of potassium dichromate (*a*) in 50 c.c. of water. Add 50 c c. of 50 per cent. (by volume) sulphuric acid, and to the cold undiluted solution add from a weighing-bottle a moderate excess of the ferrous ammonium sulphate, and titrate back with the dilute dichromate (*b*). Calculate the value of the ferrous salt in terms of dichromate.

(*d*) *Silver Carbonate.*—This is prepared as required; for each test from 140 c.c. of 0·5 per cent. silver sulphate solution by precipitation with about 4·9 c.c. $\frac{N}{1}$ sodium carbonate solution (a little less than the calculated quantity of $\frac{N}{1}$ sodium carbonate should be used; any excess of alkali carbonate prevents rapid settling). Settle, decant, and wash once by decantation.

(*e*) *Subacetate of Lead.*—Boil a pure 10 per cent. lead acetate solution with an excess of litharge for one hour, keeping the volume constant, and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide.

(*f*) *Potassium Ferricyanide.*—A very dilute solution containing about 0·1 per cent.

The Method.—Weigh 20 grms. of the glycerol, dilute to 250 c c., and take 25 c.c. Add the silver carbonate, allow to stand, with occasional agitation, for about ten minutes, and add a slight excess (about 5 c.c. in most cases) of the basic lead acetate (*e*), allow to stand a few minutes, dilute with distilled water to 100 c.c , and then add 0·15 c.c. to compensate for the volume of the precipitate, mix thoroughly, filter through an air-dry filter into a suitable narrow-mouthed vessel, rejecting the first 10 c.c., and return filtrate if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate. (In the great majority of cases 5 c c. is ample.) Occasionally a crude glycerol will be found requiring more, and in this case another aliquot of 25 c.c. of the dilute glycerol should be taken and purified with 6 c.c. of the basic acetate. Care must be taken to avoid a marked excess of basic acetate.

Measure off 25 c.c. of the clear filtrate into a glass flask or beaker (previously cleaned with potassium dichromate and sulphuric acid). Add 12 drops of sulphuric acid (1 : 4) to precipitate the small excess of lead as sulphate. Add 3·7282 grms. of the powdered potassium bichromate (*a*). Rinse down the dichromate with 25 c.c. of water, and stand with occasional shaking until all the dichromate is dissolved (no reduction will take place).

Now add 50 c.c. of 50 per cent. sulphuric acid (by volume) and immerse the vessel in boiling water for two hours, and keep protected from dust and organic vapours, such as alcohol, until the titration is completed. Add from a weighing bottle a slight excess of the ferrous ammonium sulphate (C), making spot tests on a porcelain plate with the potassium ferricyanide (F). Titrate back with the dilute dichromate. From the amount of dichromate reduced calculate the percentage of glycerol.

1 grm. glycerol equals 7·4564 grms. dichromate.

1 „ dichromate equals 0·13411 grm. glycerol.

Notes.—1. It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

2. Before the dichromate is added to the glycerol solution it is essential that the slight excess of lead be precipitated with sulphuric acid as stipulated in the process.

3. For "crudes" practically free from chlorides the quantity of silver carbonate may be reduced to one-fifth and the basic lead acetate to 0·5 c.c.

4. It is sometimes advisable to add a little potassium sulphate to insure a clear filtrate.

Instructions for Calculating Actual Glycerol Content.—1. Determine the apparent percentage of glycerol in the sample by the acetin process as described. The result will include acetylisable impurities, if any be present.

2. Determine the total residue at 160° C.

3. Determine the acetin value of the residue at (2) in terms of glycerol.

4. Deduct the result found at (3) from the percentage obtained at (1) and report this corrected figure as glycerol. If volatile acetylisable impurities are present, these are included in this figure.

Notes and Recommendations.—Experience has shown that in crude glycerol of good commercial quality the sum of water, total residue at 160° C. and corrected acetin result, comes to within 0·5 of 100. Further, in such "crudes" the dichromate result agrees with the uncorrected acetin result to within 1 per cent.

In the event of greater differences being found, impurities, such as polyglycerols or trimethylene glycol, are present. Trimethylene glycol is more volatile than glycerol; it can therefore be concentrated by fractional distillation. An approximation to the quantity can be obtained from the spread between the acetin and dichromate results of such distillates, trimethylene glycol showing by the former method 80·69 per cent., and by the latter 138·3 per cent., expressed as glycerol.

In valuing crude glycerol for certain purposes it is necessary to ascertain the approximate proportion of arsenic, sulphides, sulphites, and thiosulphates. The methods for detecting and determining these impurities have not formed the subject of this investigation.

(Signed) Otto Hehner, *Chairman.*
John Allan.
James B. M'Arthur.
W. H. Phillips.
P. Tainsh.
Frank Tate.
J. L. Buchanan, *Hon. Secretary.*

Recommendations by Executive Committee.—If the non-volatile organic residue at 160° C. in the case of a soap lye "crude" be over 2·5 per cent.—*i.e.*, when not corrected for carbon dioxide in the ash—then the residue shall be examined by the acetin method, and any excess of glycerol found over 0·5 per cent. shall be deducted from the acetin figure.

In the case of saponification, distillation, and similar glycerol, the limit of organic residue which should be passed without further examination shall be fixed at 1 per cent. In the event of the sample containing more than 1 per cent., the organic residue must be acetylated, and any glycerol found (after making the deduction of 0·5 per cent.) shall be deducted from the percentage of glycerol found by the acetin test.

British Standard Specifications for Crude Glycerins.—The following standard specifications were drawn up by the British Executive Committee on crude glycerin analysis, and approved at a general meeting of crude glycerin makers, buyers, and brokers held in London on October 3rd, 1912 :—

Soap Lyes, Crude Glycerin.—Analyses to be made in accordance with the International Standard Methods (*supra*).

Glycerol.—The standard shall be 80 per cent. of glycerol. Any crude glycerin which tests 81 per cent. of glycerol or over shall be paid at a *pro rata* increase, calculated as from the standard of 80 per cent. Any crude glycerin which tests under 80 per cent. of glycerol, but is 78 per cent. or over, shall be subject to a reduction of 1½ times the shortage, calculated at a *pro rata* price as from 80 per cent. If the test falls below 78 per cent. the buyer shall have the right of rejection.

Ash.—The standard shall be 10 per cent. In the event of the percentage of ash exceeding 10 per cent., but not exceeding 10·5 per cent., a percentage deduction shall be made for the excess calculated as from 10 per cent. at *pro rata* price, and if the percentage of ash exceeds 10·5 per cent., but does not exceed 11 per cent., an additional percentage deduction shall be made to double the amount in excess of 10·5 per cent. If the amount of ash exceeds 11 per cent. the buyer shall have the right of rejection.

Organic Residue.—The standard shall be 3 per cent. A percentage deduction shall be made of 3 times the amount in excess of the standard of 3 per cent. calculated at *pro rata* price. The buyer shall have the right to reject any parcel which tests over 3·75 per cent.

Saponification Crude Glycerin.—Analysis to be made in accordance with the International Standard Methods, 1911.

Glycerol.—The standard shall be 88 per cent. Any crude glycerin tendered which tests 89 per cent. or over shall be paid for at a *pro rata* increase calculated as from the standard of 88 per cent. Any crude glycerin which tests under 88 per cent., but is 86 per cent. or over, shall be subject to a reduction of 1½ times the shortage calculated at *pro rata* price as from 88 per cent. If the test falls below 86 per cent. the buyer shall have the right of rejection.

Ash.—The standard shall be 0·5 per cent. In the event of the ash exceeding 0·5 per cent., but not exceeding 2·0 per cent., a percentage reduction shall be made equal to double the amount in excess of 0·5 per cent. If the amount of ash exceeds 2·0 per cent. the buyer shall have the right to reject the parcel.

Organic Residue.—The standard shall be 1 per cent. A percentage deduction shall be made of twice the amount in excess of the standard of 1 per cent. calculated at *pro rata* price. The buyer shall have the right to reject any parcel which tests over 2 per cent.

APPENDIX I.

REPORTS.

MINISTRY OF FOOD: OILS AND FATS BRANCH.

Report by the Committee of Analysts on Standard Methods of Analysis of Seeds, Nuts and Kernels, Fats and Oils, and Fatty Residues.—A Committee of Analysts was appointed by the Director of Oils and Fats in November, 1918, to consider the settlement of standard methods of analysis of oil-seeds, fats, and oils. The terms of reference of the Committee were as follows :—

1. To determine the ingredients affecting the value of any of the scheduled articles.

2. To consider the usual limits of constants for good merchantable quality of the scheduled articles.

3. To arrange standard tests for all the scheduled constants for scheduled articles, and special tests.

The following took part in the deliberations of the Committee :— Otto Hehner (Chairman), John Allan, G. H. Appleyard, E. R. Bolton, J. L. Buchanan, Alfred Smetham, E. W. Voelcker, W. Ellard Woolcott.

11 Billiter Square, E.C.,
February 26, 1919.

The Director of Oils and Fats, Ministry of Food.

Sir,—The Committee of Analysts appointed by you have considered the questions embodied in the terms of reference conveyed to them at the meeting on November 13 last, and beg to submit herewith for the consideration of the Ministry of Food their report on the standard methods of analysis for oil-seeds, nuts and kernels, fats and oils, and fatty residues. They present separately schedules of the data essential in defining the commercial value of particular oils, and of some of the standards governing " good merchantable quality." Other data will probably have to be added later.

The Committee have held fourteen meetings, and those members who have not been able to be present at the meetings have collaborated by correspondence.

I am, Sir,
Your obedient Servant,
(*Signed*) Otto Hehner
(*on behalf of the Committee of Analysts*).

Part. I.—Determination of Oil in Seeds, Nuts, and Kernels.

1. Extract a weighed quantity of the sample prepared for analysis with petroleum ether [1] in a suitable apparatus for two hours. Remove the partially extracted material, dry, grind in a mortar (grinding may be facilitated by the addition of 1 gramme of fine sand), and again extract until exhausted. If the sample contains a large percentage of oil it is advisable to grind twice, extracting after each grinding. Evaporate off the solvent, dry at 100° C., and weigh. In the case of oils liable to rapid oxidation, like linseed, drying should be conducted in an inert atmosphere.

2. The extracted oil must be free from solid matter and completely soluble in petroleum ether.

3. In the case of woolly cotton-seed special attention must be paid to obtaining an average sample. The seed must either be crushed by being passed through steel rollers and then thoroughly ground in an iron mortar, or well broken and ground in a mortar.

4. Owing to the variation both in the amount and composition of the oil in cross-sections of the " meat " of copra, it is essential that the portion taken for analysis from the original sample be cut from the pieces at right angles to the rind. The copra must, therefore, be reduced by shredding or grating at right angles to the rind, or small pieces must be completely shaved down.

5. In the case of castor-seed the clean seed with the shell is ground in a mortar, which is covered to prevent loss of husk. The extraction must be more prolonged than is the case with other seeds, and is, as a rule, complete in eight hours.

Part II.—Fats and Oils.

6. In the sample of fat or oil the following constituents are first determined :—Moisture, organic dirt, ash, fatty matter (by difference) —total 100.

7. Upon the clear filtered fatty matter the following determinations are made :—Acid value, saponification value, unsaponifiable matter, iodine value.

8. The estimations and determinations shall be carried out according to the methods described below.

Moisture.—9. A U-tube, one limb of which is an ordinary narrow-bore glass tube, and the other a tube about 3 feet long and from 1¼ to 1½ inches in diameter (see appended sketch), is charged in its wider limb with soft blue Cape asbestos, which has been dried at 100° C. The wide limb is provided with a rubber stopper, through which passes a narrow tube bent at right angles. The tube, without the stopper, accurately weighed, suspended by a wire, and about 2 grms. of the well-mixed sample of oil or fat are dropped on to the asbestos, and the whole reweighed. The stopper is then inserted, and the tube which

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[1] Petroleum ether, volatile without residue at or below 60° C.

passes through the stopper is connected with a Kipp apparatus supplying hydrogen, thoroughly dried by passage through strong sulphuric acid.

10. A **U**-tube, such as is used in elementary analysis, and provided with two glass taps, is filled with glass beads which are afterwards moistened with strong sulphuric acid. This tube is accurately weighed, after having previously been filled with dry hydrogen, and is then connected with the narrow limb of the asbestos-charged tube, the latter being suspended in a beaker containing water kept at a temperature about 10° C. above the melting point of the fat. A slow current of hydrogen is now passed through the whole. When no trace of condensed moisture can be seen in the horizontal limbs of the oil tube and of the weighing tube, which is generally the case after one hour, the latter is weighed, then again attached, and a current of hydrogen allowed to pass for another hour. Minute traces of volatile organic matters, as a rule, produce a slight darkening of the sulphuric acid.

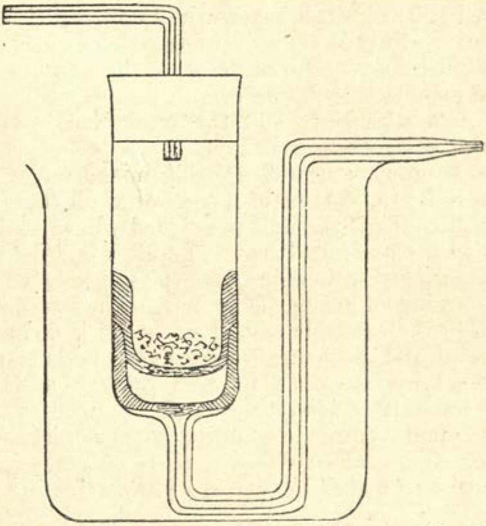

Fig. 181.—Apparatus for Estimating Moisture in Oils and Fats.[1]

11. The asbestos may advantageously be used in the form of a very porous felt paper produced by pulping the asbestos and running the pulp into a centrifugal which is lined with linen.

12. As an alternative method capable of dealing with a number of samples in one operation, stoppered weighing bottles of about the dimension of the wider limb of the **U**-tube used in the standard method may be charged with asbestos, or alternatively with strips of pleated blotting-paper or with paper pulp. These tubes are dried in a vacuum desiccator containing sulphuric acid, and kept at a pressure of 2 to

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[1] *Analyst*, July, 1920.

5 mm. After weighing, about 2 grms. of the fat or oil are placed in each tube, which is again weighed. The tubes are warmed till the fat is melted, and then replaced into the vacuum desiccator. The air is exhausted and the desiccator is kept in an incubator at 20° C. for at least forty-eight hours. The weight after that time remains practically constant.

13. The standard method is applicable to all fats and oils, whether readily oxidisable, like linseed oil, or containing high percentages of free fatty acid of low molecular weight, such as lauric.

14. In the case of fats and oils which are free from uncombined fatty acid and not readily oxidisable, the ordinary methods of drying on sand in a water-oven may often be used, provided the results are in agreement with those furnished by the standard method.

Dirt and Ash.—15. The percentage of "dirt" in a sample of oil should be arrived at by direct estimation, and not by difference.

16. In the case of a sample containing dirt of such a nature and size as to render it impossible to incorporate the whole of it uniformly throughout the sample, the whole of the sample should be strained through a 25-mesh wire sieve and the solid fragments picked out, weighed, and separately examined.

17. At least 10 grms. of the thoroughly mixed fat or oil is treated with about ten times its volume of hot paraffin oil (kerosene), the insoluble matter filtered off through a weighed filter, washed with hot kerosene, then with petroleum ether. The filter is dried in the water-oven to constant weight, incinerated, and the ash weighed.

18. The percentage of ash in the strained oil is determined.

19. The ash in the insoluble matter in the oil is deducted from the ash found in the oil, and this figure is taken as "soluble mineral matter."

Acid Value—*Definition.*—20. The acid value of a fat or oil is a measure of the free fatty acids present, and is defined as the number of mgrms. of potassium hydroxide required to neutralise the free fatty acids in 1 grm. of the fat or oil—*i.e.*, parts of potassium hydroxide which are required to neutralise the free fatty acids in 1,000 parts of the fat or oil.

Chemicals Required.—21. (*a*) Alcoholic alkali solution, $\frac{N}{10}$ and $\frac{N}{2}$ potassium or sodium hydroxide, accurately standardised. (*b*) Neutral alcohol, 94 to 95 per cent. (by volume), containing 0·2 grm. of phenolphthalein per litre. This may be conveniently prepared by redistilling industrial methylated spirits free from mineral oil over sodium hydroxide, adding the phenol-phthalein, and subsequently neutralising.

The Test.—22. The necessary quantity of the fat or oil is carefully weighed into a 250 c.c. flask, and about 50 c.c. of the alcohol are added. The mixture is gently boiled, well shaken to thoroughly dissolve out the free fatty acids, and titrated while still warm, and with constant agitation, with $\frac{N}{10}$ alkali till the pink colour is permanent on shaking for ten seconds. Towards the end of the titration the alkali should be added drop by drop in order to avoid excess until the end point is reached.

23. As a rule, 5 grms. of the sample will be found a suitable quantity, but in the case of refined fats or oils this should be increased to 10 grms. If more than 10 c.c. $\frac{N}{10}$ alkali solution are required for the test, it should be repeated with $\frac{N}{2}$ alkali.

Then if X = number of c.c. of $\frac{N}{10}$ solution,
F = weight of fat or oil taken,

$$\text{Acid value} = \frac{X \times 5{\cdot}61}{F}.$$

24. In order to express the acidity in percentages of oleic acid, the following formula should be used :—

$$\text{Oleic acid per cent.} = \frac{X \times 2{\cdot}82}{F}.$$

25. In the case of fats obtained from the kernels of the coconut group, such as coconut oil, palm-kernel oil, tucum, babassu, cohune, etc., the acidity is calculated as lauric acid, when the following formula should be used :—

$$\text{Lauric acid per cent.} = \frac{X \times 2{\cdot}0}{F}.$$

Saponification Value—*Definition.*—26. The saponification value represents the amount of potassium hydroxide required to neutralise the free and combined acid constituents of a fat or oil, and is expressed in terms of parts of potassium hydroxide per 1,000 parts of the fat or oil.

Solutions Required.—27. (*a*) $\frac{N}{2}$ hydrochloric acid accurately standardised. (*b*) An alcoholic solution of potassium hydroxide or sodium hydroxide, approximately $\frac{N}{2}$, prepared by dissolving 18 to 20 grms. of stick potassium hydroxide in not more than 10 c.c. of distilled water, and making up to 500 c.c. with 94 to 95 per cent. (by volume) alcohol, which may be prepared as in par. 21 (*b*). The solution is allowed to stand for twenty-four hours, and the clear liquid siphoned off for use. Potassium hydroxide may be replaced by sodium hydroxide, but this substitution is not desirable. The alcohol must be free from mineral oil and of such a purity as to yield a nearly colourless solution after twenty-four hours. (*c*) An alcoholic solution of phenol-phthalein, 1 per cent.

The Test.—28. About 2 grms. of the clear filtered fat are accurately weighed into a 200 c.c. flask of resistance glass, 25 c.c. of neutral alcohol added, and 25 c.c. of the alcoholic potassium hydroxide solution accurately measured run in. A like quantity of the same solution is run in, in exactly the same way, into a similar flask, together with 25 c.c. of the neutral alcohol. The flasks are connected to reflex condensers and heated, preferably in a water-bath, so that the alcohol boils briskly for thirty minutes. The flask containing the fat should be shaken with a rotary movement from time to time during the period. The contents of the flasks are then titrated while hot with the $\frac{N}{2}$ acid, after the addition of 1 c.c. of the phenol-phthalein solution.

If F = grms. of fat taken,
X = c.c. of acid required in the control experiment,
Y = c.c. of acid required to neutralise the excess of alkali in the test,

$$\text{Then saponification value} = \frac{X - Y \times 0.02805 \times 1{,}000}{F}.$$

$$\text{N.B.—The saponification equivalent} = \frac{561{,}000}{S},$$

Acid Value and Saponification Value (Combination Method).—29. The acid value and saponification value may, if so desired, be determined upon the same weight of the sample in the following manner :—

30. About 4 grms. of the clear filtered fat or oil are accurately weighed into the saponification flask, and 25 c.c. of hot alcohol containing 1 c.c. of phenol-phthalein solution, and previously neutralised, are added. The free fatty acids are titrated from a burette with the alcoholic alkali solution as used for the saponification value, warming if necessary during the titration. The number of c.c. required by the free fatty acids having been noted, such a further quantity of alcoholic alkali as will make a total of 50 c.c. is added, and the process continued as described above.

31. A blank test is made with 50 c.c. of the alcoholic alkali delivered from the identical burette, using similar quantities of all the reagents. The exact value of the alcoholic alkali having been determined with $\frac{N}{2}$ hydrochloric acid, the acid value and saponification value may be respectively calculated.

Unsaponifiable Matter.—32. Unsaponifiable matter in fats and oils includes all substances which are insoluble in water but soluble in the fat solvents specified below after alkali saponification of the fats and oils.

33. Saponify 5 grms. of the sample with 50 c.c. approximately normal alcoholic KOH, boiling under a reflux condenser for sixty minutes with occasional shaking. Transfer the alcoholic solution to a separating funnel, rinse the flask successively with 50 c.c. of methylated ether, 50 c.c. of petroleum ether, and 50 c.c. of water. Transfer the rinsings to the separating funnel, shaking well after each addition. Allow to separate, and withdraw the soap solution. Repeat the extraction of the soap solution twice, using ether and petroleum ether as before, omitting the treatment with water. The combined ethereal extracts are washed by shaking with slightly alkaline water, allowing to settle, and run through a filter into a tared flask. Wash the filter with petroleum ether, distil off the solvents, dry at 100° C., and weigh the unsaponifiable matter.

Iodine Value—34. *Reagents Required*—(*a*) *Iodine Solution.*—35. This is conveniently prepared by dissolving 7·5 grms. of iodine trichloride in acetic acid (minimum strength, 95 per cent.), and solution may be hastened by warming on a steam-bath. When dissolved, add to the solution 8·2 grms. of resublimed iodine, assist solution by heating as before, and make up to 1,000 c.c. with acetic acid (95 per cent.). The solution is standardised by means of a blank test carried out at the time that it is used, which should be at least twenty-four hours after it is made up. If the solution is heated for a short time by immersion in boiling water, it may be used immediately after cooling.

(*b*) *Sodium Thiosulphate Solution.*—36. Dissolve 24·8 grms. of the pure salt in 1 litre of distilled water. It is advisable to add 0·5 grm. per litre of sodium bicarbonate to the solution as a preservative. This solution must be standardised by titrating it against pure dry resublimed iodine, but where this is inconvenient the iodine may be liberated from potassium iodide by a known amount of potassium dichromate in the presence of hydrochloric acid. As the oxidising value of potassium dichromate does not always correspond accurately with that of an equivalent amount of iodine, the potassium dichromate to be used as described below shall first be set against pure dry iodine. The titration is carried out as follows:—Weigh 0·20 grm. of pure recrystallised $K_2Cr_2O_7$ into a 200 c.c. stoppered bottle, dissolve in 25 c.c. distilled water, add 20 c.c. 10 per cent. potassium iodide solution and 10 c.c. HCl, moisten the stopper with the KI solution, and allow to stand five minutes. Wash down the stopper with distilled water, dilute to about 100 c.c. volume, and titrate the liberated iodine with the sodium thiosulphate solution, using starch solution as indicator. A blank test, using the potassium iodide solution and hydrochloric acid alone, should be carried out, and the necessary deduction, if any, made from the previous titration.

$$0{\cdot}2 \text{ grm. } K_2Cr_2O_7 = 0{\cdot}51768 \text{ iodine.}$$

(*c*) *Potassium Iodide Solution.*—37. A 10 per cent. solution of the pure salt in distilled water.

(*d*) *Solvent.*—38. Chloroform or carbon tetrachloride to be used as a solvent for the oil. A blank test on the solvent must not show an absorption of iodine equal to more than 0·2 c.c. of the thiosulphate solution.

(*e*) *Starch Solution.*—39. Use a 1 per cent. solution of soluble starch.

Method.—40. 0·15 to 1 grm. of the sample is weighed into a wide-necked stoppered bottle of about 200 c.c. capacity; 0·15 grm. of a strongly drying oil and a proportionately larger amount for oils or fats of lower iodine value, up to approximately 1 grm. for such fats as coconut and the like. Dissolve the weighed quantity of fat or oil in 10 c.c. of the solvent (*d*) and add 25 c.c. of the iodine solution, moisten the stopper with potassium iodide solution, and allow to stand for one hour. In the case of fats having a very high iodine value like linseed, allow to stand for three hours.

41. After standing, wash the stopper and neck of the bottle down with 15 c.c. of the 10 per cent. potassium iodide solution, mix, and add 100 c.c. of distilled water, and titrate the excess of iodine with the sodium thiosulphate solution. Towards the end of the titration add about 2 c.c. of the starch solution, and shake vigorously after each addition of the thiosulphate solution until the contents of the bottle are colourless.

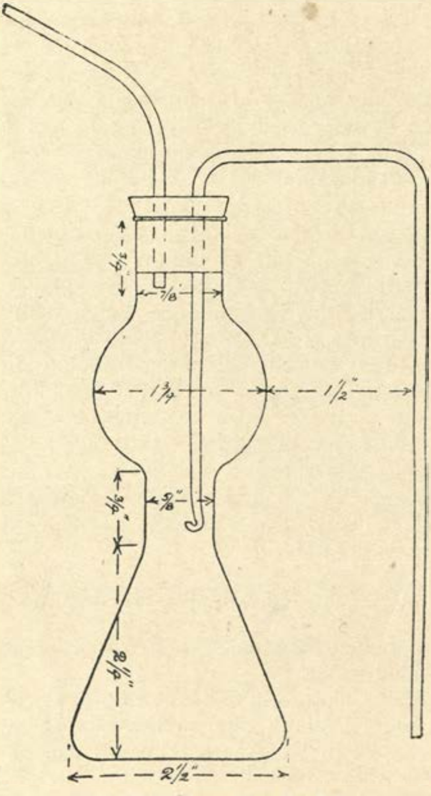

Fig. 182.—Separating Flask.[1]

42. A blank test, using 10 c.c. of fat solvent and 25 c.c. of the iodine solution, must be done with each set of estimations, or at least once daily.

43. The result is expressed as per cent. of iodine reacting with the fat.

44. *N.B.*—Where a large number of liquid oils have to be tested

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[1] *Analyst*, July, 1920.

it may be convenient to weigh them by dropping them from a small lipped tube and ascertaining the weight taken by difference, while solid fats can be arranged in small cubes on a suitably-sized glass plate and picked up with a pin which has been tared along with the whole; in this case also the weights of the successive pieces are determined by difference until the last piece has been weighed.

Specific Gravity and Viscosity.—45. In cases where it is desirable to determine the specific gravity or the viscosity of an oil or fat, the specific gravity shall be determined by the ordinary standard methods and viscosity by the Redwood viscometer.

Titer Test.—46. In cases where it is desirable to determine titer the method to be adopted is that prescribed by the Seventh International Congress of Applied Chemistry. This method is given in full in J. Lewkowitsch's "Chemical Technology of Oils and Fats," fifth edition, 1913, vol. i.

Part III.—Fatty Residues: Evaluation of Soap Stock, Acid Oils and Fatty Acids, Cotton Oil, Black Grease, and Mucilage.

47. A weighed quantity of the sample (sufficient to give from 1 to 2 grms. of fatty extract) is introduced into a separating flask as illustrated, 10 to 20 c.c. of hot water are added, followed by one drop of methyl orange and a sufficient excess of hydrochloric acid to insure the decomposition of soap; 5 grms. of salt are added, and the mixture is heated gently until the acids separate in a clear layer.

48. The contents of the flask are allowed to cool to about 30° C., and 20 c.c. of petroleum ether and the liquors are gently agitated, and water is added until the junctions of the water and ether rises to the bottom of the centre constriction. When the separation is complete the ether is blown off by means of a siphon and, if necessary, filtered into a weighed flask, 10 c.c. of petroleum ether are introduced into the separating vessel, and again siphoned off. Two further portions of 10 c.c. of petroleum ether are then used, and in these latter cases the flask is closed with a stopper, and gently inverted two or three times after each addition of ether.

49. The mixed ethereal extracts are distilled and the residue dried at 100° C. and weighed.

Report by the Committee of Analysts on Standards of Good Merchantable Quality.—Members of the Committee of Analysts: Otto Hehner (Chairman). John Allen, G. H. Appleyard, E. R. Bolton, J. L. Buchanan, Alfred Smetham, E. W. Voelcker, W. Ellard Woolcott.

11 BILLITER SQUARE, E.C.,
March 5, 1919.

TO THE DIRECTOR OF OILS AND FATS, MINISTRY OF FOOD.

SIR,—1. In the terms of reference submitted to us by you at our first meeting on November 13, 1918, we were asked to arrange standard tests for all constants and all schedules for oil seeds, nuts and kernels, and oils and fats. We have already communicated to you the results of our deliberations on this point.

2. We now forward for your consideration our report on the two other terms of reference, which we have interpreted as follows:—(i.) To determine the ingredients affecting the value of any of the scheduled articles; (ii.) to consider the usual limits of constants for good merchantable quality of the scheduled articles.

3. **Standards for Vegetable Oils.**—An official schedule for vegetable oils, home manufactured, good merchantable quality, was submitted to us embodying a blank schedule for the insertion of standards and constants under several headings. After due consideration we decided that, although all of these particulars are of interest to analytical chemists, it would not be practically useful to insert the whole of these in a contract. We, therefore, decided to limit our recommendations to those characteristics which have an immediate bearing on the commercial value of the oil.

4. We recommend the following standards for oil of "good merchantable quality" on the understanding—(i.) that such oils shall be free from foots and foreign matter (a mere compliance with the standard prescribed does not furnish proof of purity). (ii.) That an allowance should be made to the buyer or the seller for any deviation from these standards.

The figures are based on records covering, in some cases, a considerable period of years, and have been selected as representing a fair average, and as tending to raise rather than lower the existing standard.

5. We realise that other considerations actually enter into the value of different oils, specially those required for edible purposes. There is at present a very great difficulty in defining systematically such qualities as colour, turbidity, and odour, but it might be possible eventually to secure such a definition.[1]

6. **Seeds, Nuts, and Kernels ("Good Merchantable Quality").**—We have also considered the definition of "good merchantable quality" in the case of seeds, nuts, and kernels. In this case, too, we have selected the figures from records which different firms have been kind enough to make available, and have sought to establish an average which will tend to the general improvement of the product. In some cases, where the same kind of produce is imported from widely differing sources, there is necessarily a good deal of variation. Moreover, produce coming from the same source is liable to differ in standard from year to year, and at different periods of the same year.

7. We have, nevertheless, come to the conclusion that it would be a great advantage to have standards that might be applied with an allowance, over or below, to the seller or to the buyer, for all kinds of produce. We think that such standardisation, even in the case of crops varying so much as cotton-seed and linseed from place to place and

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[1] We understand that a Sub-Committee of the Oils and Fats Committee of the Food Investigation Board are now considering the question of palatability of edible oils, and that further research into the general question is in contemplation.

year to year, would tend to the improvement of the produce, and to better conditions of storage and transport. We have, therefore, given standards for one or two classes with a view to simplification.

8. The standards which we suggest are calculated on the pure produce, and assume that the determination of shell and dirt has already been carried out. The question whether the oil content of any oleiferous admixture which is not pure produce should be estimated depends on the terms of the contract, and is a commercial matter on which we are not competent to offer a recommendation. As, however, impurities are usually the same kind from the same country of origin, it might be possible to fix an average oil content, if this were required, for the foreign oleaginous admixture.

9. The data in the schedule which we propose conform to those already adopted for the West African Contract, but we have included data for other seeds, nuts, and kernels which are not covered by that document. The schedule is as follows :—

SCHEDULE.

(Oil of "good merchantable quality" shall be free from foots or foreign matter, and shall conform to the following standards.)

Oil.	Percentage of Free Fatty Acids (Oleic, except where otherwise stated).	Percentage of Moisture not exceeding –	Percentage of Unsaponifiable Matter.	Other Standards.
LINSEED OIL—				
Raw,	2	0·25	1	Iodine value (Wijs) 185.
Refined,	2	0·25	1	,, ,,
COTTON OIL—				
Crude, Indian,	2·5	0·25	1·5	
,, Egyptian,	4			
Technical Refined	0·3			
Common edible,	0·3			
Fine edible,	0·15			
GROUND-NUT OIL—				
Crude,	4	0·25	1	
Fine edible,	0·15			
SESAMÉ OIL—				
Crude,	3·5	0·25	1	
Fine edible,	0·15			
RAPE OIL—				
Crude,	1	0·25	1	Specific gravity, 0·915. Viscosity, Redwood standard.
Technical Refined	1			
Fine edible,	0·1			

SCHEDULE—*Continued.*

Oil.	Percentage of Free Fatty Acids (Oleic, except where otherwise stated).	Percentage of Moisture not exceeding—	Percentage of Unsaponifiable Matter.	Other Standards.
PALM-KERNEL OIL—				
Technical,	5 lauric.	0·25	1	
Fine edible	0·1 ,,			
CASTOR OIL—				
Pharmaceutical,	1	0·25	1	Specific gravity, 0·963.
Firsts,	1			
Seconds,	4			
SOYA OIL—				
Crude,	2·5	0·25	1	
Fine edible,	0·15			
MAIZE OIL—				
Crude,	3	0·25	2	
Fine edible,	0·15			
COCONUT OIL (Technical)—				
Cochin quality,	1 lauric	0·25	1	
Ceylon,	2			
Copra,	4			
Fine edible,	0·1			

SCHEDULE OF STANDARDS FOR SEEDS, NUTS, AND KERNELS.

	Oil Content.	Percentage of Free Fatty Acids[1] in Extracted Oil.
Babassu,	66	2 (lauric).
Castor-seed,	47	1
Copra,	66	2 (lauric).
Cotton-seed, Egyptian type,	22	3
,, Indian type,	18	2
Benni-seed, gingelly, or sesamé,	54	3
Decorticated ground-nuts,	48	6
Undecorticated ground-nuts,	37	2
Linseed,	38	1·5
Mowrah,	58	..
Palm-kernel,	52	6 (lauric).
Rape-seed,	43	2
Shea-nuts,	46	10
Soya,	17	2

[1] Calculated as oleic unless otherwise stated.

10. **Analysis of Feeding Stuffs.**—The method of analysis of oil-cake is prescribed under the Fertilisers and Feeding Stuffs Act. As the use of petroleum ether as a solvent has been agreed upon for oleaginous seeds, nuts, and kernels, we should like to suggest that the Board of Agriculture be invited to consider the use of the same solvent for oil-cake, on the ground that ether at present prescribed as the solvent has a tendency to extract from oleaginous materials non-fatty substances.

11. The schedules referred to us did not include animal fats, but we are willing to investigate these if desired.

We are, Sir,

Your obedient Servants,
(*Signed*)
(*The Committee of Analysts.*)

APPENDIX II.

VITAMINES AND FATS.

A RECENT summary of the present state of our knowledge on the subject of vitamines is given in the *Chemische Umschau*, 1920, xxvii., 147. The name originated with Funk (*Z. Unters. Nahr. Genussm.*, 1917, xxxiii., 448), whilst Meyer termed them "accessory nutrients." According to Tschirch (*Schweiz. Med. Woch.*, 1920, p. 21), they belong to a special kind of enzymes, which play a part in the metabolism of nucleic acids, whilst Ullmann is of opinion that they are also concerned in the absorption of carbohydrates.

The vitamine of rice was isolated by Susuki, Shimamura, and Odake from the husk of rice by extraction with alcohol, precipitation with phosphotungstic acid, and decomposition of the precipitate with barium hydroxide. They termed this substance "crude oryzanine." By heating it for two hours with 3 per cent. hydrochloric acid, they obtained an α-acid, $C_{10}H_8NO_4$ and a β-acid, $C_{18}H_{16}N_2O_9$. According to Funk, however, rice vitamine is a tetra-basic acid, and these two acids have the formulæ $C_{28}H_{19}O_9N_5$ and $C_{26}H_{20}O_9N_4$. Rice contains about 0·4 to 0·5 per cent. of oryzanine.

Schick (*Deutsch. med. Woch.*, 1920, xlvi.) classifies vitamines into the following groups :—

1. *Antineuritic vitamines*, which are mainly found in cereal germs, eggs, leguminous pods, yeast, flesh, green vegetables, and bran.
2. *Antirachitic vitamines*, occurring in butter, cream, cod-liver oil, beef fat, flesh, meat, and green vegetables.
3. *Antiscorbutic vitamines*, which are found in fruits, such as oranges and lemons, seeds freed from germs, the cabbage tribe, flesh, and milk.

The necessity for vitamines increases with acceleration of the vital metabolism, more being required in cold weather, heavy muscular exertion, and in the period of growth.

The experiments of Zuntz (*Pfluger's Arch. Physiol.*, lxxxii., 557) and of Hindhede (*Skand. Arch. Physiol.*, 1919, xxxix., 78) have shown that, although fats may be replaced isodynamically by equivalent quantities of carbohydrates, they possess specific antirachitic action, and that they are absolutely essential to growth. Feeding experiments on animals also showed that carbohydrates could not take the place of fats. The fats which promote growth include butter, egg oil, cod-liver oil, and rape-seed oil, and these fats can to a certain extent replace one another. No vitamines have as yet been found in lard, olive oil, almond oil, linseed oil, maize oil, or margarine. From these results it follows that the nutritive values of fats should no longer be exclusively based upon their relative heats of combustion.

This conclusion as to the absence of fat-soluble vitamines from lard is not borne out by the experiments of Daniels and Loughlin, who have detected appreciable quantities of the growth-promoting constituent both in lard and cotton-seed oil (*J. Biol. Chem.*, 1920, xlii., 359). This fat-soluble constituent may be extracted by means of alcohol from carrots and from cabbage, and such extract was found capable of supplying the growth-promoting factor to rats fed upon a diet not containing fat-soluble vitamine (Zilva, *Biochem. J.*, 1920, xiv., 494).

It has been shown by Drummond (*Biochem. J.*, 1919, xiii., 95) that the vitamine contained in certain oils and fats, such as butter and whale oil, is destroyed by long-continued exposure to temperatures as low as 37° C., and rapidly at 100° C., the decomposition not being due to oxidation or hydrolysis. The vitamine could not be isolated in a pure condition, and was not identified with any recognised constituent of the oils.

It may be mentioned that the term " vitamines " as applied to these factors is misleading, since they do not appear to be amines at all. Like the enzymes, they are apparently the material substrata of specific forms of energy, and their chemical nature has not been definitely ascertained.

A method for the quantitative estimation of the growth-promoting factor has been devised by Williams (*J. Biol. Chem.*, 1920, xlii., 259). A definite amount of the solution under examination is added to 100 c.c. of a stock culture medium containing asparagine and ammonium sulphate, and the mixture made up to 110 c.c. and sterilised. It is then inoculated with 1 c.c. of a freshly-prepared suspension of yeast containing 0·3 grm. of fresh yeast per litre, and incubated for 18 hours. Further growth is then stopped by the addition of a little formaldehyde, any wild yeast skimmed off, and the growth of the selected yeast collected in a Gooch crucible, washed with water and alcohol, and dried at 100° C. A control test is made simultaneously, and the weight of yeast obtained deducted from that given in the actual test. The " vitamine number " of the material is the number of mgrms. of yeast produced by the addition of 1 grm. of the material.

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BELL AND BAIN, LIMITED, PRINTERS, GLASGOW.

Fig. 105.—Soft Lard Crystals (magn.).

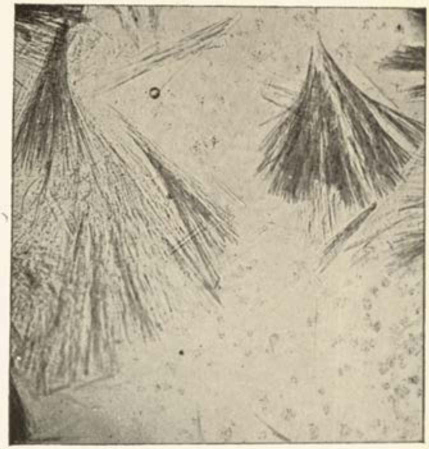

Fig. 106.—Flare Lard Crystals (magn.).

Fig. 107.—Crystals from a Mixture of Lard and Beef Fat (magn.).

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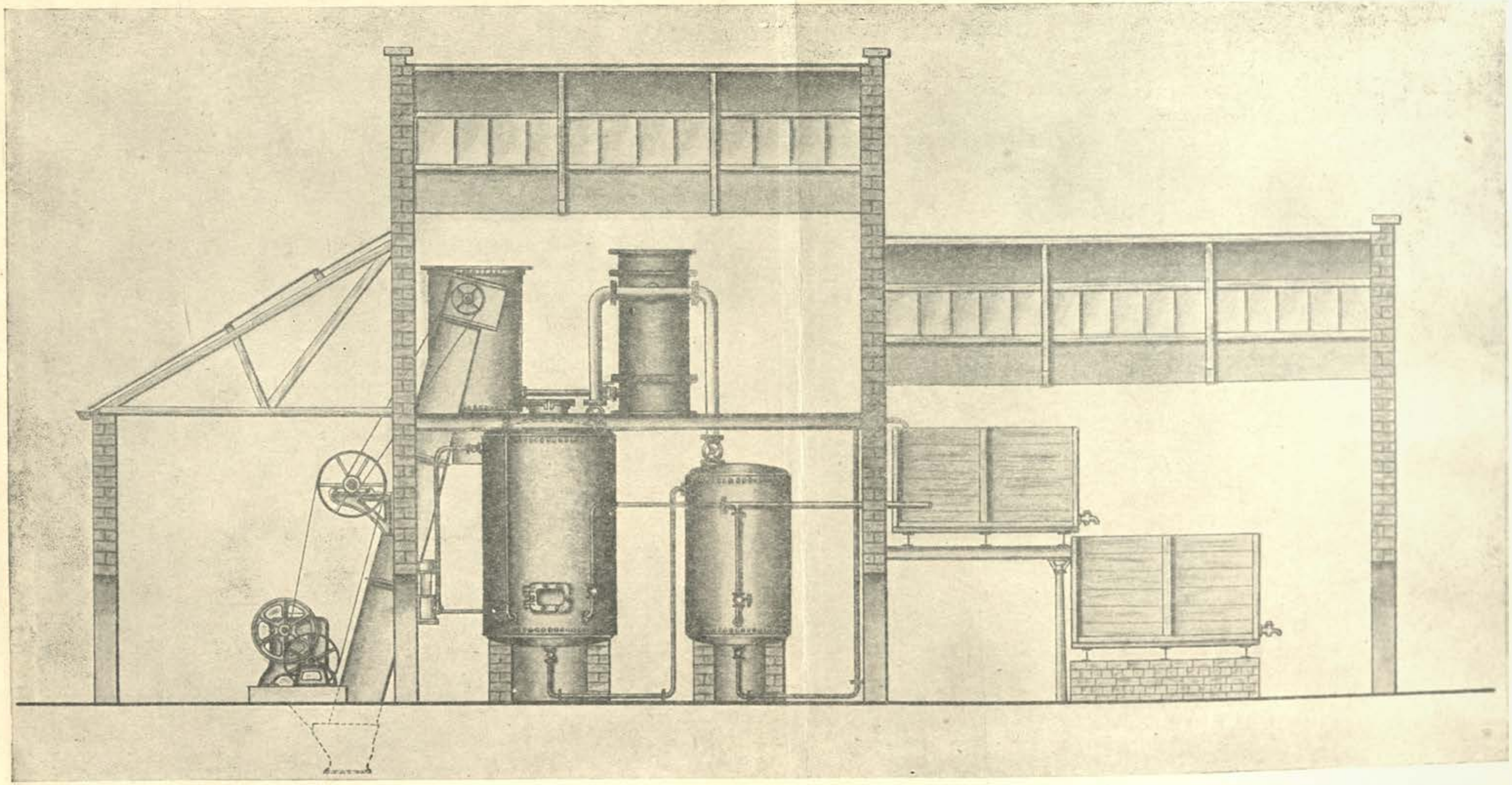

Fig. 90.—Arrangement of Plant for Extracting Oil from Bones.

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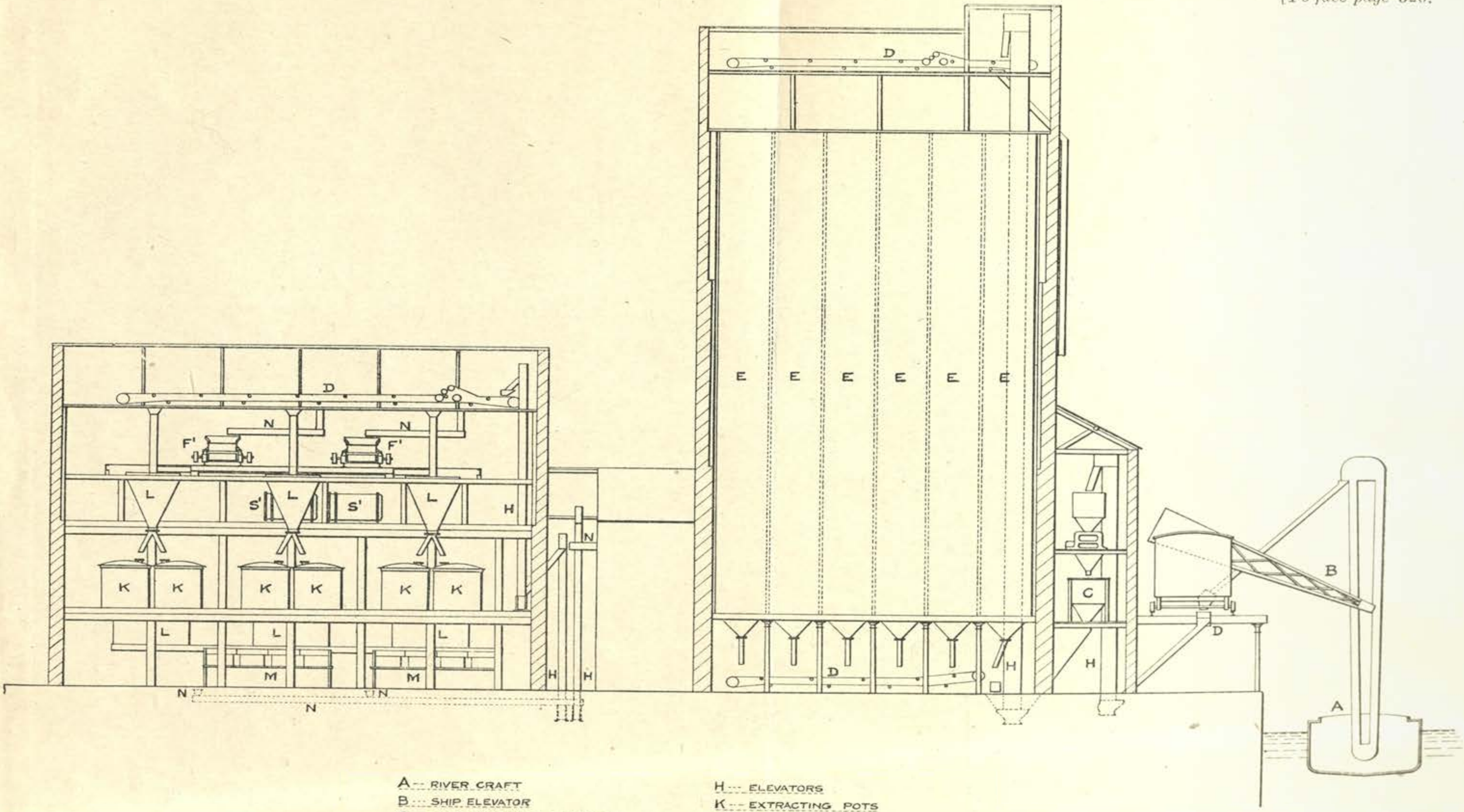

A -- RIVER CRAFT
B -- SHIP ELEVATOR
C -- SEED CLEANING SCREENS
D -- BAND CONVEYORS
E -- GRAIN SILOS
F' -- FLAKING ROLLS
H -- ELEVATORS
K -- EXTRACTING POTS
L -- BINS
M -- DRYING MACHINES
N -- SCREW CONVEYORS
S' -- CONDENSERS

Fig. 77.—Cross-Section of Solvent Extraction Plant, treating 600 Tons per Week.