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THE CHEMISTRY OF LINSEED OIL

J. NEWTON FRIEND

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CHEMICAL MONOGRAPHS

EDITED BY A. C. CUMMING, D.Sc.

The Chemistry of Linseed Oil

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The progress of Chemistry is so rapid that it is becoming a matter of ever-increasing difficulty to keep abreast of the modern developments of the science. The volume of periodical literature is so enormous that few can hope to read, far less assimilate, all that is published. The preparation of summaries has therefore become a necessity, and has led to the publication of various well-known journals devoted to the abstraction of original papers. For obvious reasons, however, these do not fully supply the wants of advanced students and research workers, and it is now generally recognised that monographs on special subjects are also needed.

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The Chemistry of Linseed Oil. By J. Newton Friend, D.Sc., Ph.D., F.I.C., Carnegie Gold Medallist.

Other Volumes to follow.

THE CHEMISTRY OF LINSEED OIL

BY

J. NEWTON FRIEND

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TO

ALDERMAN C. J. WHITEHEAD, J.P.

CHAIRMAN OF THE HIGHER EDUCATION COMMITTEE
OF THE CITY OF WORCESTER, THIS MONOGRAPH
IS

DEDICATED

IN APPRECIATION OF HIS KEEN INTEREST IN
SCIENTIFIC AND TECHNICAL EDUCATION.

AUTHOR'S PREFACE

THE Chemistry of Oils is a study of peculiar interest. Not only does it afford a wide field for research by the pure chemist, but it also offers a tempting bait to the industrial or technical chemist. The subject has not received the attention it deserves from the student of chemistry, and it is hoped that this little monograph will serve to stimulate interest in it. The thoughtful reader cannot peruse these pages without realising what a number of important problems still require elucidation, and teachers seeking suitable subjects for research for their more promising pupils should experience no difficulty in finding them here.

It is of course impossible to deal with the subject as thoroughly as one could wish within the restricted limits of a small monograph, but explanatory notes and full references are given, which, it is hoped, will prove a useful feature of the work. In almost every case the original memoirs have been consulted, and in this connection the Author desires to express his sincere thanks to Mr F. W. C. Clifford, Librarian of the Chemical Society, for his unfailing courtesy and assistance. To the Editor, Dr Alex. C. Cumming, the Author is glad to have this opportunity of expressing sincere thanks for many useful criticisms and suggestions.

J. NEWTON FRIEND.

July 1917.

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THE CHEMISTRY OF LINSEED OIL

SECTION I.

INTRODUCTION.

What is an Oil?—An oil may be defined as a combustible organic liquid, greasy to the touch, usually lighter than but insoluble in water, soluble in alcohol, benzene, ether, and other common organic solvents. A **fat** is a solid oil, and thus bears the same relation to the latter as ice to water. The difference is merely one of temperature, and usually the term fat is reserved for such as are solid at and above 20° C., whilst oils are liquid below that point. The hardest fats melt at about 50° C. **Waxes** are hard organic solids, capable of taking a polish, and when melted yield combustible oily liquids. Neither oils nor liquid waxes have any definite boiling-points, since at temperatures somewhat above 100° C. they decompose evolving acrid vapours.

As is usually the case with popular terminology, these words are frequently employed irregularly. Thus sulphuric acid is known as "oil of vitriol," although, save in its appearance, it possesses no single property of a true oil. Again, sealing-wax is not a wax but a resin, the name having been handed down from the times when a genuine wax was used for sealing correspondence.

Classification of Oils and Waxes. — When an attempt is made to classify oils and waxes many difficulties arise, so much so that no perfect scheme appears to be possible. For many purposes the following arrangement has proved useful:—

1. Animal and vegetable waxes.
2. Mineral oils and waxes.
3. Essential oils.
4. Animal oils and fats.
5. Vegetable oils and fats.

Animal and vegetable waxes are well exemplified by spermaceti and carnaüba wax respectively. They differ from vegetable oils in that they are ethereal salts of organic acids and the higher monohydric alcohols such as cetyl and myricyl. Thus spermaceti, which occurs in the oil obtained from the heads of whales, consists of cetyl palmitic ester or cetyl palmitate. Japanese wax, however, is an exception for it consists essentially of palmitin,[1] the glyceride of palmitic acid and hence, from the chemical point of view, is a fat (*vide infra*).

Mineral oils and waxes consist mainly of hydrocarbons. They are found free in nature as petroleum or rock oil, but are also obtained industrially by the distillation of oil shale. The lower members of the series are gases or liquids of low boiling-point, whilst the higher are known as vaselines and paraffin wax. The intermediate members constitute the petrols, benzolines and naphthas, illuminating or paraffin oils, and lubricating or machine oils.

Essential oils are those which impart to plants, etc., their odour, taste, or other characteristic properties. Well-known examples are cinnamon, clove, and orange oils.

Animal oils, as their name implies, are obtained from animals, mostly marine. Cod liver oil, whale oil, and sperm oil are familiar examples. In chemical composition most of these resemble vegetable oils and consist essentially of glycerides of organic acids. Sperm oil, however, is exceptional as it contains only a negligible quantity of glycerol.[2] What the nature of its alcohols may be is at present unknown.

Vegetable oils are glycerides of organic acids and admit of classification into three groups known respectively as—

(*a*) Non-drying oils, *e.g.*, olive and rape oils,
(*b*) Semi-drying oils, *e.g.*, cotton seed and soya bean oils,
(*c*) Drying oils, *e.g.*, linseed and hempseed oils,

according to their power of "setting" or "drying" when spread in thin films exposed to the air on plates of non-absorbent material, such as glass or metals. In these circumstances a drying oil may be expected to set in a few days at room temperature, whilst a non-drying oil will remain liquid for an indefinite time. Semi-drying oils are intermediate between these two.

It should be borne in mind, however, that the distinction between drying, semi-drying, and non-drying oils is mainly one of degree, for there is reason to believe that all fixed oils, whether vegetable or animal, sooner or later set to solid elastic products similar to those yielded by drying oils, provided the temperature is sufficiently high (120°-160° C.).[3] Even at ordinary temperatures a similar drying takes place in the course of years.[4]

The present monograph is concerned with the chemistry of a typical drying oil, namely *linseed oil.*

SECTION II.

THE MANUFACTURE OF LINSEED OIL.

Linseed is the name given to the seeds of the flax-plant *Linum usitatissimum* which, though a native of Central Asia, is now grown in large quantities in the Argentine, India, U.S.A., Canada, and Russia. To a smaller extent the plant is cultivated in Morocco and in various parts of Europe, including England and Ireland. The importance of the flax-growing industry is evident from a consideration of the accompanying table, in which is detailed the tonnage of linseed produced in five of the principal flax-growing areas.[1]

Production of Linseed (expressed as tons).

Year.	Argentine.	India.	U.S.A.	Canada.	Russia.
1903	937,601	481,367	682,513	21,100	461,314
1906	825,764	353,400	626,500	25,588	540,500
1909	716,515	297,700	487,817	120,829	558,360
1912	1,130,000	641,200	701,825	528,505	650,000

The rapid increase in the production of Canadian linseed is particularly noteworthy.

The seeds are brown in colour, from 4 to 8 mg.

in weight,[2] and of specific gravity ranging from 1·12 to 1·15. When pure they contain from 36 to 42 per cent. of oil,[2,3] practically all of which may be extracted by the aid of suitable solvents.

Extraction of Linseed Oil. — In commercial practice[4] it is usual to extract the oil from linseed by pressure. To this end the sifted seed is crushed to a "meal" by passage between grooved rollers, heated in a "kettle" to about 70° C., packed in bags and submitted to a pressure of some two or more tons per square inch in a hydraulic press.

Analyses of Linseed Cake.

	Oil.	Water.	Albuminoids.	Digestible carbohydrates.	Woody fibres.	Mineral matter.	Sand.
American	10·06	9·30	33·37	31·84	10·37	5·06	...
,, .	9·10	10·25	34·63	30·63	9·84	5·55	0·45
Bombay .	15·63	7·35	31·37	25·55	9·60	10·50	2·90
Calcutta .	9·83	9·25	33·25	34·82	5·70	7·15	2·20
Russian .	9·70	11·70	35·25	30·35	7·70	5·30	0·60

The cakes left behind in the press still contain from 9 to 16 per cent. of oil and are very valuable as food for cattle, as is evident from the table of analyses,[5] in which the "albuminoids" represent the total nitrogen × 6·25, whilst the "digestible carbohydrates" include all non-nitrogenous organic matter save woody fibre and oil.

The effect of heating the meal before pressing is probably twofold. Not only does it help to coagulate albuminous material and thus prevent its expression with the oil, but on the other hand the heat increases the solvent properties of the oil, with the result that the expressed product is darker in colour and possesses a stronger odour than oil pressed out of meal in the cold. In the preparation of the purest oil such as that required by artists, the meal is cold-pressed without being kettled.

If linseed is crushed and moistened, hydrogen cyanide is slowly liberated in consequence of the action of an enzyme on a cyanogenetic glucoside. When the oil is cold-pressed, the resulting cake is liable to behave like the crushed linseed, a fact which has an important bearing on its suitability as a cattle food in view of the poisonous character of hydrogen cyanide. Dilute acids are found to prevent the enzyme from working, $N/100$ hydrogen chloride completely inhibiting the action, whilst $N/1000$ acid produces a marked retardation. Since the acidity of the human stomach is approximately $N/20$, and that of animals is hardly likely to be appreciably lower, it would appear that the cold-pressed cake may be safely fed to non-ruminants. The case of ruminants is more difficult. If, however, the linseed meal is heated prior to pressing the enzyme is thereby destroyed; so that the ordinary commercial hot-pressed cakes may be safely used for cattle food.[6]

It is interesting to note in passing that linseed grown in temperate climes (England, in particular) is less dangerous than oriental seed.[7]

Refining Linseed Oil.—The crude oil obtained from the press contains a number of undesirable impurities, chief amongst which are water, mucilaginous material, glycerides of organic acids, and organic colouring matter. At one time the oil was exposed in shallow vessels to sunlight for some months, and this process is still employed for artists' oil. The sunlight bleaches the chlorophyll and allied compounds which cause the deep colour of the crude oil, so that a lighter product results.

For ordinary commercial purposes, however, the crude oil is usually tanked, heated to about 70°-80° C., and allowed to stand. Any albumen that has escaped from the seed is coagulated and sinks with other solid impurities to the bottom of the tank. About 2-3 per cent. of fairly concentrated sulphuric acid is now added to the oil, and the two are thoroughly mixed and allowed to stand some hours. The mucilaginous matter becomes charred, and as it sinks to the bottom it carries other suspended impurities with it. Water, too, is absorbed by the acid, which, after about twenty-four hours, has collected at the bottom of the tank leaving a purer oil above.

Extraction of Linseed Oil by Solvents.—Linseed oil is sometimes extracted by treating the meal with a suitable solvent, such as benzoline, in which the oil dissolves. The solvent is afterwards distilled off and used over again. In this case practically the whole of the oil content of the seed may be extracted. In expressing the oil from meal, the more fluid portions, consisting of triglycerides of unsaturated organic acids, escape first, so that the residue left in the cake will contain a proportionately higher percentage of the less fluid oily constituents, namely, the triglycerides of saturated organic acids. These latter, however, are readily extracted along with the more fluid unsaturated glycerides when a solvent is used, so that solvent-extracted oil may be expected to exhibit inferior "drying" properties to that obtained by pressure from the same kind of seed. That such is often the case has been shown by Mastbaum,[8] but apparently the difference is not always appreciable.[2]

SECTION III.

THE CHIEF CONSTITUENTS OF LINSEED OIL.

BEFORE passing on to consider the general properties of linseed oil it is advisable to deal with those of its chief constituents. When pure, linseed oil is essentially a mixture of the triglycerides of oleic, linolic, and linolenic acids. Small quantities of glycerides of saturated organic acids are also present, but as they are of minor importance they will not receive detailed treatment.

GLYCEROL.

Glycerol, known in commerce as *glycerine*, was discovered by Scheele towards the close of the eighteenth century when saponifying olive oil with litharge in the preparation of lead plaster. The name glycerol is due to Chevreul who drew attention to the analogies existing between it and alcohol.

Glycerol is readily prepared by saponification of fats or oils with mineral acid or superheated steam.

When pure it is a thick, viscid liquid, sweet to the taste, but possessed of no colour or odour. It is soluble in water which it absorbs readily and with which it mixes in all proportions, a contraction in volume and slight heat evolution being observed. On cooling below 0° C. it solidifies to a white, crystalline mass melting at 17° C. Its specific gravity at 15° C. is 1·265. At 290° C. it boils without appreciable decomposition, and readily distils unaltered with superheated steam. It is soluble in alcohol but not in ether.

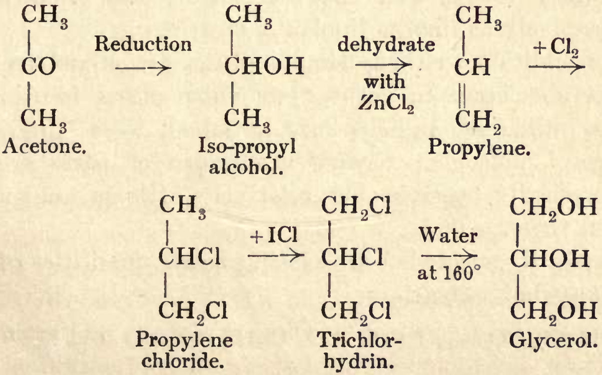
In aqueous solution alkaline permanganate oxidises it quantitatively to carbon dioxide and oxalic acid.

$$C_3H_5(OH)_3 + 3O_2 = (COOH)_2 + CO_2 + 3H_2O.$$

With sulphuric acid and bichromate of potash glycerol is oxidised to carbon dioxide and water, whilst warming with concentrated sulphuric acid causes evolution of acrolein.

$$C_3H_5(OH)_3—2H_2O = CH_2 : CH . CHO.$$

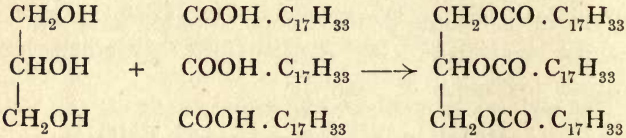
The constitution of glycerol follows from its preparation from trichlorhydrin upon heating with excess of water at 160° C. Thus—



$$\underset{\text{Acetone.}}{\begin{matrix}CH_3\\|\\CO\\|\\CH_3\end{matrix}} \xrightarrow{\text{Reduction}} \underset{\text{Iso-propyl alcohol.}}{\begin{matrix}CH_3\\|\\CHOH\\|\\CH_3\end{matrix}} \xrightarrow[\text{with } ZnCl_2]{\text{dehydrate}} \underset{\text{Propylene.}}{\begin{matrix}CH_3\\|\\CH\\\|\\CH_2\end{matrix}} \xrightarrow{+Cl_2}$$

$$\underset{\text{Propylene chloride.}}{\begin{matrix}CH_3\\|\\CHCl\\|\\CH_2Cl\end{matrix}} \xrightarrow{+ICl} \underset{\text{Trichlorhydrin.}}{\begin{matrix}CH_2Cl\\|\\CHCl\\|\\CH_2Cl\end{matrix}} \xrightarrow[\text{at } 160°]{\text{Water}} \underset{\text{Glycerol.}}{\begin{matrix}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{matrix}}$$

Glycerol is thus seen to be a trihydric alcohol, and capable of forming three classes of esters, namely, tri-, di-, and mono-glycerides. In nature only triglycerides are found, except that traces of the others appear to occur as the result of hydrolysis in rancid oils and fats. Triglycerides of organic acids are, as has already been mentioned (see p. 3), the essential constituents of vegetable and animal oils. Thus, for example, *olein* which occurs in tallow, olive oil, and is also present in linseed oil, is the triglyceride of oleic acid.



$$\begin{array}{lclcl} CH_2OH & & COOH . C_{17}H_{33} & & CH_2OCO . C_{17}H_{33} \\ | & & & & | \\ CHOH & + & COOH . C_{17}H_{33} & \longrightarrow & CHOCO . C_{17}H_{33} \\ | & & & & | \\ CH_2OH & & COOH . C_{17}H_{33} & & CH_2OCO . C_{17}H_{33} \\ \text{Glycerol.} & & \text{Oleic acid.} & & \text{Olein.} \end{array}$$

Other triglycerides with which we shall have occasion to deal are those of linolic, linolenic, stearic, palmitic, lauric, and myristic acids, and known respectively as linolin, linolenin, stearin, etc.

In addition to these simple glycerides mixed triglycerides occur in nature[*] in which either two or three different radicles are attached to a single glycerol molecule. Several isomerides of these are theoretically possible, but relatively little is known about them.

Schlicht[1] succeeded in isolating small quantities of linolo-palmito-stearin—

$$C_3H_5(O . CO . C_{17}H_{31})(O . CO . C_{15}H_{31})(O . CO . C_{17}H_{35}),$$

---

[*] In fact, there is good reason to believe that many of the supposedly simple triglycerides occurring in oils are really mixed (see p. 58).

from a sample of La Plata oil exposed to a temperature of −8° to −10° C. Traces of other mixed triglycerides were also obtained, which were probably the following: dioleo-stearin, linolo-distearin, and oleo-linolo-palmitin.

Triglycerides are readily saponified by alcoholic potash yielding potassium soaps and free glycerol. Thus—

$$\underset{\text{Olein.}}{C_3H_5O_3(CO.C_{17}H_{33})_3} + 3KOH = \underset{\text{Glycerol.}}{C_3H_5(OH)_3} + \underset{\text{Potassium oleate.}}{3C_{17}H_{33}.COOK.}$$

The amount of potash, expressed as grams of KOH, required to saponify in this manner 1000 grams of triglyceride is known as the **saponification value**, and, as we shall see later (see p. 34), affords a useful check on the purity of an oil.

The process of saponification does not proceed quite as simply as the above equation would imply. Lewkowitsch[2] concluded that it probably occurred in stages, the intermediate products being diglycerides and monoglycerides. This is apparently supported by recent work on the subject.[2]

OLEIC ACID.

Oleic acid, $C_{18}H_{34}O_2$, or $C_{17}H_{33}.COOH$, is the most important member of the series of olefine monocarboxylic acids to which the general formula $C_nH_{2n-1}.COOH$ is given, and which possess one ethylenic linkage in the chain. It occurs as the glyceride olein in most animal and vegetable oils, and is present in this form in linseed oil.

Oleic acid is most conveniently prepared from tallow by saponification with potassium hydroxide and precipitation of the lead salt with lead acetate. Extraction with ether, in which lead oleate dissolves, and addition of hydrochloric acid to the solution, liberates the free acid, which may be purified by fractional distillation under reduced pressure.

When quite pure oleic acid is a colourless substance, without action on litmus. It is apparently dimorphous, one form melting at about 16° C. (Kirschner)[3] and the other at 6·5° C. (Partington).[3] The boiling-point of the acid *in vacuo* has been variously given as 153° C. (Krafft and Weilandt)[4] and 130° C. (Caldwell and Hartley).[5] Other values are 166° C. at a pressure of 0·25 mm. (Fischer and Harries)[6] and 223° C. at 10 mm. (Krafft and Nördlinger).[7] Density 0·898 at 15° C.[8]

When exposed to sunlight and air for prolonged periods, oleic acid assumes a yellow colour and becomes rancid, various decomposition products such as formic, acetic, azelaïc, and dihydroxystearic acids resulting.[9] At 120° C. the acid may be oxidised in a current of air,[10] its density increasing simultaneously. It absorbs sulphur at 130°-150° C., but hydrogen sulphide is not evolved until a temperature of 200°-300° C. is reached, which suggests that addition products are first formed. This is interesting in view of the analogous behaviour of rubber.[11]

Treated with alkaline permanganate solution, dihydroxystearic acid is formed,[12] whilst when heated with hydrogen iodide and amorphous phosphorus,[13] or with hydrogen iodide alone,[14] stearic acid results.

From an alcoholic solution of iodine and mercuric chloride, oleic acid readily absorbs iodine. Theoretically, two atoms of iodine are absorbed at the double bond per molecule of acid, that is 90·07 grams of iodine per 100 grams of acid. The former figure is known as the **Iodine Value** (see p. 37), and is an excellent criterion of the purity of the acid.

Constitution of Oleic Acid.—That oleic acid is unsaturated, possessing one ethylenic grouping is evidenced by its power of absorbing two atoms of iodine or bromine,[15] yielding, in the latter case, dibromostearic acid. This, on reduction with zinc and hydrochloric acid is converted into oleic acid again.

Further, as already stated, oxidation with permanganate in dilute alkaline solution yields dihydroxystearic acid,[12] in accordance with Hazura's Rule[16] that under the above conditions unsaturated acids absorb as many hydroxyl groups as they possess free valencies, yielding hydroxy acids which contain the same number of carbon atoms as the original acids.

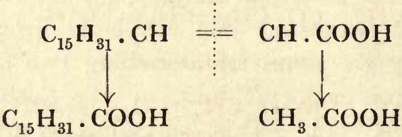
Assuming stearic acid and its dibromo and dihydroxy derivatives to have the following formulæ—

$$C_{17}H_{35}.COOH,\ \ C_{17}H_{33}Br_2.COOH,$$

$$\text{and}\ \ C_{17}H_{33}(OH)_2.COOH,$$

it follows that oleic acid must be represented by $C_{17}H_{33}.COOH$. The next problem is to determine where the double bond occurs. Denoting the carboxylic carbon as 1, the next adjacent carbon atom as 2, and so on, it is evident that many isomerides are theoretically possible, namely those with the double bond between atoms 2 and 3, or between 3 and 4, and so on.

By heating oleic acid with fused caustic potash, palmitic and acetic acids result.[17] This would suggest that the double bond lies between the second and third carbon atoms, thus—



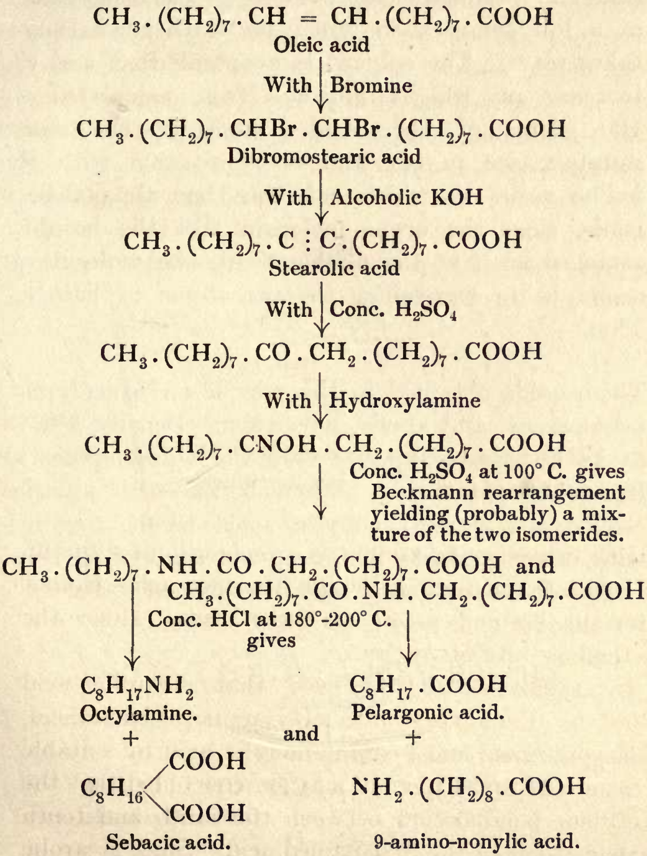
$$\begin{array}{ccc} C_{15}H_{31}.CH & = & CH.COOH \\ \downarrow & & \downarrow \\ C_{15}H_{31}.COOH & & CH_3.COOH \end{array}$$

Palmitic acid.
Acetic acid.

But an isomeride known as *iso-oleic acid* splits up in a similar manner, although the two acids cannot have the double bond in the same place. Hence the method is untrustworthy.

In 1894 Baruch[18] showed that stearolic acid could be decomposed into octylamine, sebacic acid, pelargonic acid and 9-amino-nonylic acid by suitable treatment, from which it may be concluded that the acetylene bond occurs between the ninth and tenth carbon atoms of the first-named acid. Since stearolic acid is readily obtained from oleic acid,[19] Baruch concluded that the double bond in this latter acid likewise occurs between the same carbon atoms.

The reasonableness of this assumption will be evident from a consideration of the following scheme:—



$$CH_3.(CH_2)_7.CH = CH.(CH_2)_7.COOH$$

Oleic acid

$$\Big\downarrow \text{With Bromine}$$

$$CH_3.(CH_2)_7.CHBr.CHBr.(CH_2)_7.COOH$$

Dibromostearic acid

$$\Big\downarrow \text{With Alcoholic KOH}$$

$$CH_3.(CH_2)_7.C \vdots C.(CH_2)_7.COOH$$

Stearolic acid

$$\Big\downarrow \text{With Conc. } H_2SO_4$$

$$CH_3.(CH_2)_7.CO.CH_2.(CH_2)_7.COOH$$

$$\Big\downarrow \text{With Hydroxylamine}$$

$$CH_3.(CH_2)_7.CNOH.CH_2.(CH_2)_7.COOH$$

$$\Big\downarrow$$

Conc. H_2SO_4 at 100° C. gives Beckmann rearrangement yielding (probably) a mixture of the two isomerides.

$$CH_3.(CH_2)_7.NH.CO.CH_2.(CH_2)_7.COOH \text{ and } CH_3.(CH_2)_7.CO.NH.CH_2.(CH_2)_7.COOH$$

$$\Big\downarrow \qquad \Big\downarrow$$

Conc. HCl at 180°-200° C. gives

$$C_8H_{17}NH_2$$

Octylamine.

$$+$$

$$C_8H_{16}\begin{cases} COOH \\ COOH \end{cases}$$

Sebacic acid.

and

$$C_8H_{17}.COOH$$

Pelargonic acid.

$$+$$

$$NH_2.(CH_2)_8.COOH$$

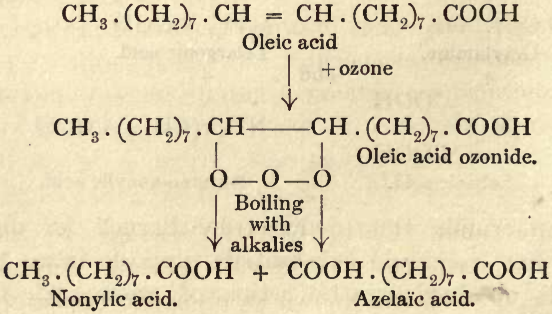
9-amino-nonylic acid.

The formula thus deduced by Baruch for oleic acid has received substantial support from the results obtained by the action of ozone upon the acid.[20] A weighed quantity of the acid is dissolved in some suitable solvent, such as hexane or acetic acid, and a stream of ozonised oxygen passed through at a low temperature until no further absorption takes place. The solvent is evaporated off and the increase in weight noted. This, calculated to 100 grams of oleic acid constitutes the **ozone number** (see p. 44), and is comparable with the iodine value to which reference has already been made, since the ozone molecule, like the halogen, attaches itself at the double bond, one molecule of ozone being equivalent to two atoms of halogen. Thus—

$$O_3 = I_2.$$

The ozonide obtained in this way is a viscous liquid, transparent, and almost colourless. Density 1·0218 at 18° C. Stable up to 80°-90° C., it decomposes at higher temperatures. When boiled with alkalies azelaïc and normal nonylic acids result, together with other products that need not concern us here.

This decomposition is readily explained if Baruch's formula for oleic acid is accepted. Thus—



$$CH_3 . (CH_2)_7 . CH = CH . (CH_2)_7 . COOH$$

Oleic acid

$$\Big\downarrow + \text{ozone}$$

$$\underset{\displaystyle O - O - O}{CH_3 . (CH_2)_7 . \overset{|}{CH} - \overset{|}{CH} . (CH_2)_7 . COOH}$$

Oleic acid ozonide.

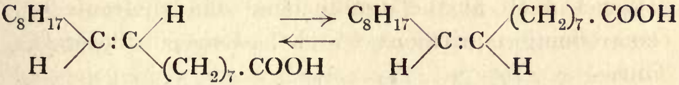
$$\Big\downarrow \text{Boiling with alkalies} \Big\downarrow$$

$$CH_3 . (CH_2)_7 . COOH + COOH . (CH_2)_7 . COOH$$

Nonylic acid. Azelaïc acid.

Baruch's formula may thus be regarded as established.[21]

Stereo-isomerism.—The presence of the double bond in the chain renders stereo-isomerism theoretically possible. The isomeride is known under the name of *elaïdic acid,* and is a crystalline body, m.pt. 51° C. It results when oleic acid is acted upon by nitrous or nitric acid.[22] The formulæ ascribed to the two acids are—



Oleic acid. Elaïdic acid.

Olein, the triglyceride of oleic acid (see p. 13), occurs in olive oil, tallow, and many other oils and fats of vegetable and animal origin. It is present in small quantity in linseed oil (see p. 56). At ordinary temperatures it is a faintly yellow liquid, solidifying at −4° to −5° C. Density 0·900 at 15° C. Iodine value 86·1.

Olein readily absorbs ozone, yielding a thick, colourless oil analogous in properties and composition to the ozonide of oleic acid.[23]

Nitrous acid converts olein into its stereo-isomeride *elaïdin.*

LINOLIC ACID.

Linolic acid, $C_{17}H_{31}.COOH$, belongs to the series of open chain acids of general formula $C_nH_{2n-3}.COOH$, and known as di-olefine carboxylic acids. It contains two ethylene linkages, and occurs in linseed oil as the triglyceride *linolin* along with *linolenin*, the two esters being originally regarded as one and known as *linolein*, the mixture of free acids being termed *linoleic acid*. Hazura[16] was the first to show that linolein is a mixture and designated its constituents as linolin and linolenin, which names are still employed.

Linolic acid readily combines with bromine to yield a crystalline tetrabromide,[16, 24] $C_{17}H_{31}Br_4 . COOH$, m.pt. 114° C., from which the free acid is regenerated on reduction with zinc and hydrogen chloride in alcoholic solution. This affords a convenient method of preparing the pure acid from the mixture of acids obtained on hydrolysing hempseed or poppy-seed oil.

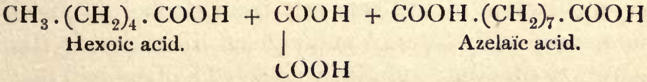
Linolic acid is an oily liquid of density 0·9026 at 18° C. It boils at 228° C. under a pressure of 14 mm.,[25] and is readily soluble in alcohol and ether. Its iodine value is 181·4, and corresponds to the absorption of four atoms of iodine per molecule of acid. Absorption of oxygen takes place when the acid is exposed to the air, a solid resinous body resulting. Reduction with hydriodic acid and phosphorus at 200° C. yields stearic acid,[26] $C_{17}H_{35} . COOH$, the same reaction taking place with hydrogen in the presence of a catalyst. Oxidation with alkaline permanganate solution yields a tetrahydroxystearic acid, more commonly known as sativic acid,[16, 25] $C_{17}H_{31}(OH)_4 . COOH$, m.pt. 173° C.

Constitution of Linolic Acid.—That linolic acid contains two double bonds within its molecule is evident from its iodine number, and from the fact that with bromine a tetrabromide is formed. Further evidence is afforded by Thieme,[29] who prepared the ozonide and showed that it contained two molecules of ozone, each molecule attaching itself, as in the case of oleic acid, at a double bond. The problem, therefore, is to determine in what parts of the linolic acid molecule the double bonds occur. This was accomplished by Goldsobel in 1906.[27] Owing to the difficulty of getting the pure acid he used sativic acid, m.pt. 173° C. (*vide supra*), the relation of which to linolic acid is perfectly well known. Oxidation of this acid with dilute alkaline permanganate solution yielded azelaïc, oxalic, and hexoic (or caproic) acids. This may readily be explained if the assumption is made that the double bonds of linolic acid occur between the ninth and tenth and the twelfth and thirteenth carbon atoms. Thus—

$$CH_3.(CH_2)_4.CH = CH.CH_2.CH = CH.(CH_2)_7.COOH$$

Linolic acid.

which, on oxidation, breaks at the double bonds into—



$$\underset{\text{Hexoic acid.}}{CH_3.(CH_2)_4.COOH} + \begin{array}{c} COOH \\ | \\ COOH \end{array} + \underset{\text{Azelaïc acid.}}{COOH.(CH_2)_7.COOH}$$

Goldsobel has more recently confirmed the above formula by optical methods.[28]

Stereo-isomerism.—The presence of the double bonds renders stereo-isomerism possible, similar to that existing between oleic and elaïdic acids, to which reference has already been made. Evidence has been adduced in favour of the existence of two stereo-isomerides of linolic acid in linseed oil,[25] but the subject is at the moment a matter of dispute, to enter into which is beyond the province of this monograph.

LINOLENIC ACID.

Linolenic acid, $C_{17}H_{29}.COOH$, is the only well-known member of the tri-olefine monocarboxylic acid series of general formula, $C_nH_{2n-5}.COOH$. It was first identified by Hazura [16] as one of the constituents of linoleic acid. It readily yields a crystalline hexabromide of m.pt. 177° C.,[30] thus affording a convenient method of separating the acid from the mixture obtained by the saponification of linseed oil. Reduction with zinc and hydrogen chloride in alcoholic solution yields the free acid in two stereo-isomeric modifications designated as α and β respectively.[31] Of these only α-linolenic acid appears to exist in any quantity in linseed oil,[33] from which it may be isolated in the pure state by fractional crystallisation of the zinc salt from alcohol, in which it is very soluble, and subsequent liberation by the addition of dilute sulphuric acid. The free acid may be further purified by recrystallisation from petroleum spirit at $-80°$ C.

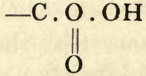
Erdmann and Bedford,[32] who prepared the acid in a very pure condition in the above manner, state that it is a colourless, oily liquid of density 0·9046 at 20° C. After standing for a few days the density of their specimen rose to 0·9248, and, after the lapse of five weeks, to 0·963. Its iodine value ranged from 269 to 278 (theory requires 273·8). On bromination the theoretical yield of linolenic hexabromide $C_{17}H_{29}Br_6 . COOH$ was obtained. The acid boils at 230°-232° C. at 17 mm. pressure,[34] and its iodine value is 274. It readily absorbs oxygen on exposure to air, acrolein being evolved.[35] As linolenic acid is even more readily oxidised than linolic acid, it is evident that the higher the percentage of linolenin in an oil the greater is the "setting" power[36] (see p. 65). Oxidation with alkaline permanganate-solution results in the formation of two hexahydroxystearic acids known as linusic (m.pt. 201°-203° C.)[34] and iso-linusic (m.pt. 171°-173° C.)[34] acids respectively.[37] The fact that two isomeric linusic acids were obtained in this way by the oxidation of the free organic acids from linseed oil led Hazura to assume that two isomeric linolenic acids were present in the original oil. He never succeeded in isolating them, however, and Rollett[34] considers that there is not sufficient evidence to justify the assumption of the existence of an iso-linolenic acid in linseed oil.

Constitution of Linolenic Acid.—The existence of a hexabromo-derivative of linolenic acid suggests the presence of three double bonds in the acid molecule, and this is confirmed by the iodine and ozone values.[38]

The actual positions of the double bonds were first determined by Goldsobel[27, 28] who suggested the formula—

$$\begin{aligned}&CH_3.CH_2.CH = CH.CH_2.CH\\&\qquad = CH.CH_2.CH = CH.(CH_2)_7.COOH.\end{aligned}$$

This was subsequently confirmed by Erdmann and Raspe[38] who ozonised both the free acid and its ethyl and methyl esters. The acid itself yielded, in chloroform solution at −20° C., a perozonide containing ten extra atoms of oxygen, that is, three molecules of ozone attached one at each of the three double bond positions, and one atom of oxygen attached to the carboxylic acid group, thus—



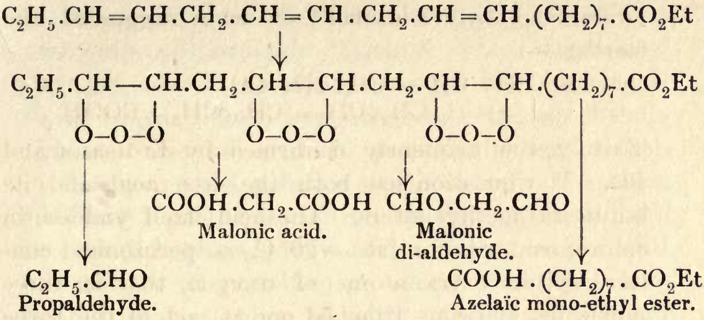
$$—C.\underset{\underset{O}{\|}}{O}.OH$$

In hexahydrotoluene, however, the normal ozonide, containing only nine atoms of oxygen or three molecules of ozone, was obtained.

The perozonide on being heated with excess of water on the water-bath yielded azelaïc acid and its mono-aldehyde, of composition $COOH.(CH_2)_7.COOH$ and $CHO.(CH_2)_7.COOH$ respectively. From this it was concluded that the carboxylic half of the linolenic acid molecule has the same constitution as the corresponding portion of oleic acid.

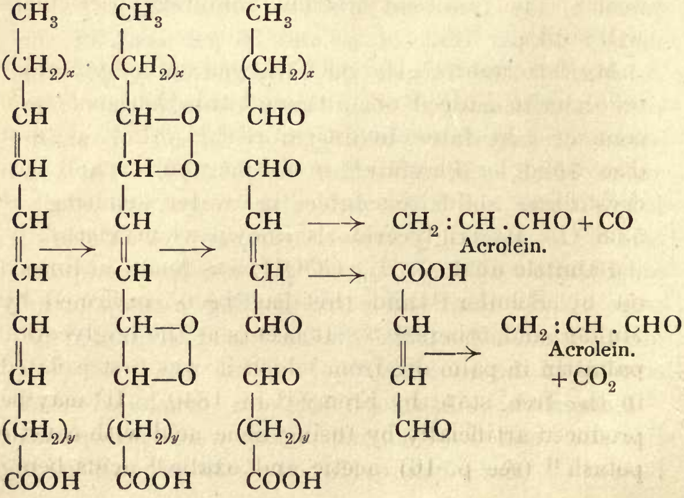
The ozonide of linolenic ethyl ester was decomposed with cold water and the following products found: propyl aldehyde, malonic acid and its aldehydes, azelaïc mono-ethyl ester and its corresponding aldehyde.

Assuming that Goldsobel's formula is correct, it is easy to account for these reactions as follows:—



Stereo-isomerism.—Mention has already been made of the fact that two stereo-isomerides of linolenic acid, namely *α*- and *β*-forms are recognised by Erdmann and Bedford.[31] These bear the same relation to one another as oleic and elaïdic acids (see p. 17). Both stereo-isomerides result when linolenic hexabromide is reduced with zinc and hydrogen chloride in alcoholic solution, the free acid mixture containing approximately 25 per cent. of *α*- and 75 per cent. of the *β*-form.[33] The former on bromination yields the pure hexabromide;[32] the latter absorbs only four atoms of bromine, yielding a viscid oil of iodine value 109·3, and molecular weight 516. The low iodine value and high molecular weight are attributable to partial polymerisation or formation of anhydrides. *β*-linolenic acid perozonide decomposes more slowly than the corresponding *α*-compound.[38] Most, if not all, of the linolenic acid in linseed oil consists of the *α*-variety.[33]

Isomerism. — Although Hazura concluded that linolenic and iso-linolenic acids were present in linseed oil, since upon oxidation of the organic acids he obtained two linusic acids, he never succeeded in isolating them.[37] Rollett[34] obtained the same two linusic acids in a precisely similar manner, but concluded that the evidence was insufficient to prove definitely the existence of two isomeric linolenic acids. The question has recently been reopened in an interesting manner by Salway,[35] who found that linolenic acid and the free organic acids of linseed oil evolve acrolein vapour on oxidation by exposure to oxygen at 100° C. This, he points out, is difficult to explain if the linolenic acid molecule is constituted according to Goldsobel's formula. If, however, the acid be regarded as a derivative of hexatriene, the reaction might well take place as follows, a dioxygenide being first formed,[39] the central double bond remaining unoxidised on account of its having, in all probability, a relatively greater stability:



Since different specimens of linolenic acid were found to yield varying quantities of acrolein, Salway regards it as conceivable that the ordinary acid is a mixture of two isomerides, one having the constitution suggested by Goldsobel, the other being a derivative of hexatriene as above.

Further research on this interesting problem is eminently desirable.

SATURATED ORGANIC ACIDS.

The saturated organic acids present in linseed oil as triglycerides are higher members of the acetic acid series of general formula, $C_nH_{2n+1} . COOH$. As they occur only in small amounts and play no essential part in the general behaviour of the oil towards chemical reagents, a detailed description of these acids is not necessary. The following particulars will suffice.

Myristic acid, $C_{13}H_{27} . COOH$, was stated by Mulder to occur in linseed oil, although this has not been confirmed by later investigators.[43, 46] It was first discovered by Playfair[44] in nutmeg butter, and is a crystalline solid, insoluble in water, melting at 53·8° C. Its triglyceride is known as **myristin.**

Palmitic acid, $C_{15}H_{31} . COOH$, was found in linseed oil by Schüler,[42] and this has been confirmed by Mulder and others.[43, 46] It occurs as the triglyceride **palmitin** in palm oil, from which it was first isolated in the free state by Fremy[40] in 1840. It may be produced artificially by fusing oleic acid with caustic potash[17] (see p. 16), acetic and oxalic[41] acids being simultaneously produced. The pure acid yields colourless, needle-shaped crystals melting at 62·6° C.

Stearic acid, $C_{17}H_{35}.COOH$, occurs at the triglyceride **stearin** in many animal and vegetable fats. It may be obtained by reduction of oleic acid (see p. 15) since it contains the same number of carbon atoms. When pure it is a white crystalline solid, melting at 69·3° C. It was first shown to be present in linseed oil by Unverdorben.[42] Mulder could not detect it in his experiments, but later investigators have done so.[43]

Arachidic acid, $C_{19}H_{39}.COOH$, occurs as **arachin** in arachis oil, and is stated by Haller [43] to be present in small quantity in linseed oil. It melts at 77° C.[45]

SECTION IV.

PROPERTIES AND REACTIONS OF LINSEED OIL.

ORDINARY commercial linseed oil is a light, yellowish-brown liquid of characteristic but not unpleasant odour. Since it is a natural product and subject to all the variations of soil and climate, of the particular variety of seed and its ripeness at the time of extraction, it follows that considerable variation may be expected in its composition, chemical behaviour, and general physical properties.

The **density** of raw linseed oil varies slightly according to its origin, but the following figures relating to samples of best Baltic and best Calcutta oils respectively may be regarded as fairly representative.[1]

Oil.	Density at			Coefficient of expansion with rise of temperature.
	0° C.	15° C.	50° C.	
Baltic .	0·94444	0·93368	0·90986	0·00076
Calcutta .	0·94208	0·93179	0·90847*	0·00074

* Calculated.

According to the Standard Specifications adopted by the U.S. Government[2] on 25th August 1913, the specific gravity[3] of raw linseed oil expressed from North American seed should not vary beyond the following limits:—

Sp. gr. at 15° C. 0·932 to 0·936
Sp. gr. at 25° C. 0·927 to 0·931

As will be seen later, when linseed oil is exposed to the air it gradually absorbs oxygen and increases simultaneously in density. For this reason oil that has been kept for prolonged periods, unless very specially preserved from contact with air, usually exhibits a greater density than fresh oil. If, however, the air is rigidly excluded no such difference will ordinarily occur with the pure oil. This is well exemplified by the following figures[4] relating to American oil:—

Oil.	Specific gravity at 15° C.	Refractive index at 25° C.
1. Fresh sample	0·9347	1·4800
Same sample after 2 years	0·9346	1·4802
2. Fresh sample	0·9331	1·4797
Same sample after 2 years	0·9330	1·4800

It is thus evident that, under favourable conditions, pure raw oil may be kept for an indefinite time without appreciable change. If the oil is not pure the density frequently alters slightly in consequence of the settling out of the impurities.

The **coefficient of expansion** of the oil with rise of temperature does not appear to have been determined very frequently. The mean value 0·00075 from the table on p. 29 may be taken as representative, and is closely similar to values that have been obtained for other oils.[5, 6]

The **refractive index** is a valuable indication of the purity of linseed oil; indeed, some authorities place more reliance upon it than on the iodine value (*vide infra*).[7] The refractive index is lowered by the presence of free organic acids and most animal and vegetable oils. The index is raised, on the other hand, by polymerisation, oxidation, as also by the presence of mineral or of rosin oil (see pp. 76, 80).

Linseed oil differs from most other vegetable oils in remaining liquid at 0° C. and below. Certain varieties of oil such as those from North Russia remain clear at −14° C.[7] Adulteration with other oils raises the temperature at which turbidity appears. When heated in the absence of air linseed oil thickens in consequence of polymerisation, the density showing a notable increase. In the presence of air polymerisation likewise occurs, coupled with rapid oxidation (see Section VI.).

When many vegetable oils are heated in vacuo a portion distils until a temperature is reached at which the whole mass froths, when further distillation becomes impossible. The weight of distillate obtained per 100 grams of oil is termed the **distillation number,** and a close connection is observable between this and the setting power of the oil. This is evident from the following data[39]:—

Oil.	Distillation number.	Oil.	Distillation number.
Drying Oils:—		*Semi-drying Oils:—*	
Tung (Chinese)	0·0	Soya bean . .	25·4
Linseed . .	16·2-16·4	Cotton-seed .	33·6
Hempseed .	20·5		
Walnut . .	23·8-24·0	*Non-drying Oils:—*	
Poppy-seed .	24·5-25·0	Rape. . .	35·6
		Castor . .	48
		Olive . .	54

It is instructive to compare these results with those in the tables on pp. 40-44, in which further distinctions between drying and non-drying oils are detailed.

When the temperature of an oil is raised, increasing quantities of vapour are evolved, and the temperature at which these become inflammable is known as the **flash point.** The approximate values for a few oils are as follows:—

Linseed oil . . .	240° C.
Rosin oil . . .	155°-160° C.
Paraffin burning oils . .	40° C.
Turpentine and rosin spirit .	35°-40° C.

It will be observed that the flash point of rosin oil is considerably lower than that of linseed oil. This fact renders the detection of rosin and other low flash point oils quite easy if they are present in appreciable quantities as adulterants of linseed oil.

THE ACETYL VALUE.

When an oil containing a hydroxylated acid radicle is heated with acetic anhydride, one acetyl group enters the molecule for each hydroxyl group present. For example, sativic acid, $C_{17}H_{31}(OH)_4 . COOH$, has four such groups, and its triglyceride *sativin* has, in consequence, twelve. When heated with acetic anhydride, therefore, twelve acetyl groups are introduced, thus—

$$\underset{\textbf{Sativin.}}{C_3H_5[OCO . C_{17}H_{31}(OH)_4]_3} + \underset{\textbf{Acetic anhydride.}}{6(C_2H_3O)_2O}$$
$$= C_3H_5[O . CO . C_{17}H_{31}(OC_2H_3O)_4]_3 + 6H_2O.$$

The product, washed free from acetic acid, is saponified with alcoholic potash, acidulated with sulphuric acid and steam distilled. The acetic acid in the distillate is estimated by titration with potash; the weight (in grams) of KOH required per 1000 grams[10] of the original oil is known as the **acetyl value.**

For oils perfectly free from hydroxy acids the acetyl value is nil, and the figure obtained for any particular oil is frequently a useful indication of its purity or otherwise. Linseed oil has a low acetyl value, which, however, is increased on oxidation. The following figures are given, amongst others, by Lewkowitsch[8] as the *true* acetyl values (*vide infra*) of the oils concerned :—

Linseed oil .	4·0	Palm oil . .	18
Olive „ .	10·6	Neatsfoot .	22
Rape „ .	14·7		

In the case of oils containing volatile acids, the acetyl value obtained by the foregoing method is obviously too great by the amount of volatile acid present. To obtain the *true* acetyl value, therefore, it is necessary to determine the volatile acids for the original oil by saponifying and subsequently steam distilling after acidulation, the volatile acids in the distillate being estimated as above by titration with potash. The number of c.c. of $N/10$KOH required to neutralise the volatile acids from 2·5 grams of oil is known as the **Reichert value**[9]; from 5·0 grams of oil, the **Reichert-Meissl value**. For linseed oil and most common vegetable oils these values are negligible.

LINSEED OIL AND THE ALKALIES.

Free organic acids are frequently present in small quantities in oils, and can easily be estimated by dissolving the oil in alcohol and titrating with dilute alcoholic potash, using phenolphthalein as indicator. The weight of KOH required per 1000 grams of oil is known as the **acid value.**[9]

When linseed oil is heated with alcoholic potash saponification ensues. The weight of potash required to saponify 1000 grams of oil is known as the **saponification value.**[9] For the sake of comparison the values usually found for several of the more common commercial oils are given in the table on p. 40.

The saponification value affords a useful method of checking the purity of an oil. Thus, for example, linseed oil usually contains about 0·8 per cent. of unsaponifiable matter (see pp. 60-63), but this is proportionately increased if there has been adulteration with mineral oil or rosin oil, since these latter are not affected by alcoholic potash.

LINSEED OIL AND HYDROGEN.

Hydrogen gas under ordinary conditions appears to have no appreciable action on linseed oil,[10] but in the presence of a catalyst the gas is absorbed, the unsaturated acid radicles being converted into the corresponding saturated ones containing the same number of carbon atoms. As catalysers, finely divided metals are particularly suitable. Nickel,[11] platinum,[12] colloidal palladium,[13] and mixtures of different metals[14] have been tried, but the first named is mostly used for commercial purposes.

The weight of hydrogen absorbed by 100 grams of oil is known as the **hydrogen number**, and may conveniently be determined as follows.[15]

Finely divided nickel is deposited on pumice by saturating with a suitable nickel compound and reducing with hydrogen. This serves as the catalyst, and is placed in a vessel heated to 170°-180° C. in an oil bath. Linseed oil is dropped upon the pumice and a known volume of hydrogen introduced. Excess of the latter is estimated by passing over copper oxide.

The method is too laborious for commercial purposes, but is highly interesting from a theoretical standpoint. The hydrogen value thus obtained is comparable with the iodine and ozone numbers described below.

Mannich and Thiele[64] have recently drawn attention to the interesting fact that the presence of animal charcoal greatly increases the hydrogen absorption capacity of palladium. An efficient catalyst is obtained by shaking powdered animal charcoal with palladium chloride solution, and hydrogenating until no more gas is absorbed. The powder is washed and dried, and may be kept unaltered until required. It is added to the oil either with or without a solvent, and when hydrogenation or **hardening** of the oil is complete, the mixture admits of being filtered off without leaving any trace of metal in the fat. This is a particular advantage in those cases when the hydrogenation of an unsaturated oil is undertaken for comestible purposes. The results in the accompanying table[64] have been obtained for various oils, and if they are compared with those in the table on p. 40, it will be observed that saturation with hydrogen of the unsaturated acid radicles is fairly complete, as indicated by the fall of the iodine values of the oils concerned to a negligible quantity.

Original Oils.	Properties of the hydrogenated or hardened oils.		
	Melting-point °C.	Iodine value.	Saponification number.
Linseed . .	68	0·2	189·6
Poppy . .	70·5	0·3	191·3
Almond . .	72	0·0	191·8
Arachis . .	64–64·5	0·0	191·6
Olive . . .	70	0·2	190·9

The saponification numbers remain much the same, as is to be expected; the melting-points rise markedly, the oils being converted into fats. Hence the technical term "hardening."

LINSEED OIL AND IODINE.

Iodine is but slowly absorbed by linseed oil at the ordinary temperature. Hübl[16] found, however, that by dissolving the oil in a suitable solvent, such as chloroform or carbon tetrachloride, and adding a solution of iodine and mercuric chloride in 95 per cent. alcohol, iodine is absorbed fairly rapidly during the first two hours, and more slowly afterwards. In about twenty hours absorption is complete. By taking a known quantity of iodine and estimating with thiosulphate the excess remaining behind when the reaction is complete, the amount absorbed by 100 grams of oil may readily be determined. This is known as the **iodine value**, and its determination is of exceptional importance to the oil chemist. It is generally assumed that a chloro-iodo addition compound is formed, one atom each of chlorine and iodine attaching themselves to the carbon atoms at each double bond, thereby yielding saturated derivatives. Thus, in the case of oleïc acid, the following reactions are believed to take place: [17]—

$$HgCl_2 + 2I_2 = HgI_2 + 2ICl$$

$$ICl + H_2O = HCl + HIO$$

$$\underset{\text{Oleic acid.}}{C_{17}H_{33}.COOH} + HIO = C_{17}H_{33}I.OH.COOH$$

$$C_{17}H_{33}I.OH.COOH + HCl = C_{17}H_{33}I.Cl.COOH + H_2O$$

and, in part of the mixture,

$$C_{17}H_{33}I.Cl.COOH = C_{17}H_{32}I.COOH + HCl.$$

Several modifications of the Hübl process have been proposed, notably those of Wijs[18] and Hanus.[19] On the respective merits of these much has been written, but a discussion of the subject does not lie within the scope of this monograph.

The iodine values of different samples of linseed oil exhibit considerable variation, due to corresponding variation in the relative amounts of unsaturated organic acids. Since most other vegetable oils, particularly those which for reasons of cheapness might be used for adulteration purposes, have a considerably lower iodine value than linseed oil, the determination of this figure affords a useful clue to the purity or otherwise of the oil. According to the U.S. Specifications for 1914,[2] the iodine value of linseed oil from North American seed should not fall below 178. No maximum value is fixed, although the previous year a maximum of 190 was stipulated.

Values ranging from 170 to 204 have been obtained by different investigators,[20] and the tendency of late years has been for the iodine value to rise on account of the greater care now exercised in marketing a purer seed.

Oxidation depresses the iodine value, so that old oils usually yield low values, although, if special precautions are taken to shield them from air and light, they may usually be kept unchanged for an indefinite period when quite pure.

This is well exemplified by the figures given by Sheppard.[21]

	Iodine Value.
1. Fresh Sample . . .	. 187·9
Same sample after 2 years .	. 187·5
2. Fresh Sample . . .	. 186·1
Same sample after 2 years .	. 185·9

For most purposes a mean iodine value of 175 may be accepted as a reasonable figure for raw linseed oil. It is important to bear in mind, however, that the iodine value does not necessarily of itself prove the purity or otherwise of a given sample of oil. Thus a high figure does not indisputably point to a pure oil, since many fish oils have a high iodine value, and may in consequence have been introduced as adulterants. Neither does a low figure of necessity condemn an oil, since old, partially oxidised linseed oil, and oil that has polymerised through heating, give low iodine values (see Sect. VI.) even when otherwise perfectly pure.

In certain cases pressed linseed oil appears to have a higher iodine value than that extracted by solvent.[22] Some such variation may reasonably be expected, since it is the more fluid, unsaturated portion of the oil that escapes under pressure, whilst with a solvent practically all the oil, saturated and unsaturated, is dissolved out. The variation, however, is not always appreciable.[4]

For the sake of comparison the iodine values of several of the more common vegetable oils, together with their densities and saponification numbers, are given in the following table. The figures, it must be remembered, are simply mean values, and any particular sample of oil may show considerable variation from these and yet be of undoubted purity.

Oil.	Density 15° C.	Saponification number.	Iodine value.
Linseed . .	0·932-0·936	189-195	170-200*
Tung (Chinese)	0·940-0·945	190-197	166-176
Hempseed .	0·925-0·932	190-195	146-160
Poppy-seed .	0·925-0·932	190-195	135-137
Walnut . .	0·925-0·927	192-197	146-150
Maize . .	0·923-0·928	187-190	118-123
Cotton-seed .	0·923-0·925	190-195	100-110
Soya bean .	0·923-0·925	190-195	120-130
Sunflower seed	0·924-0·936	190-195	120-130
Olive . .	*c.* 0·92	*c.* 190	80-110
Rape . .	*c.* 0·92	*c.* 180	80-110
Castor . .	0·96-0·97	*c.* 180	80-90

* For Baltic oil Ingle[26] has obtained values as high as 204, and for La Plata oils values as low as 168.

Of the above oils the first five exhibit marked drying properties, the next two are semidriers, whilst the final three are non-drying oils. It will be observed that the iodine value rises with the drying power.[23] The significance of this relationship will be discussed more fully in the sequel (see p. 65).

It is interesting to note, in passing, that a numerical connection appears to exist, in the case of oils such as the above which consist of triglycerides of saturated and unsaturated monocarboxylic acids, between the refractive index (n_t), density (d_t), both at t° C., saponification number (V), and iodine value (I). This relationship is expressed as follows:[63]—

$$(n_t^2-1)/(n_t^2+2)\times 100/d_t$$
$$= 33{\cdot}07+0{\cdot}00075\,(\mathrm{I})-0{\cdot}01375\,(\mathrm{V})+0{\cdot}002(t-15).$$

LINSEED OIL AND BROMINE.

When bromine is added to linseed oil dissolved in cooled ether, or preferably in ether acidified with glacial acetic acid,[24] a precipitate of mixed bromides is obtained[25] which, when washed with ether, dried and weighed, usually amounts to 35-45 per cent. of the weight of the oil taken. The precipitate contains some 56 per cent. of bromine and thus lies between hexabromlinolenin (Br = 62·3 per cent.), and tetrabromlinolin (Br = 52·2 per cent.), from which it is concluded that it very possibly consists of brominated mixed triglycerides.[25] The melting-point lies between 140° and 145° C.[25, 26] The presence of other oils does not hinder the reaction. For example, if linseed oil is mixed with olive oil, which latter yields no precipitated bromides, the same quantity of precipitate is obtained as if the linseed oil were brominated alone.

The following amounts of precipitated bromides have been obtained by different investigators with various oils:—

Oil.	Per cent. Bromides.
Linseed (Hehner and Mitchell[25])	23·86-25·8
Do. (Ingle[26])	33·7 -48·1
Do. (Sutcliffe[27])	41·6 -49·3
Hempseed (Sprinkmeyer and Diedrichs[28])	8·82
Walnut[25]	1·42-1·9
Do.[28]	2·22
Tung[25]	nil
Cotton-seed[25]	nil
Olive[25]	nil

If the weight of precipitated bromides obtained from a given sample of linseed oil falls below 20, adulteration may fairly safely be affirmed.

The interaction of bromine and the oil results in the evolution of heat, and the rise in temperature bears some relation to the extent of unsaturation of the organic acid radicles. It is commonly known as the heat of bromination or the **bromine thermal value**, this latter term being preferable for the reason given below. This figure was obtained by Hehner and Mitchell[29] by dissolving 1 gram of oil in 10 c.c. of chloroform and adding 1 c.c. of bromine, the change in temperature being recorded by a delicate thermometer. Since bromine is an awkward liquid to manipulate, it is sometimes dissolved in a solvent such as chloroform or carbon tetrachloride prior to its addition to the oil.[30] The bromine thermal values of several oils as determined by Hehner and Mitchell[29] are given in the accompanying table. It will be observed that the product of these values and the factor 5·5 gives a close approximation to the iodine values of the oils concerned.

Oil.	Bromine thermal value °C.	Bromine thermal value ×5·5.	Iodine value (Hübl).
Linseed . .	30·4	167·2	160·7
Cotton-seed .	19·4	106·7	107·13
Rape . .	18·4	101·2	88·33
Castor . .	15·0	82·5	83·77
Olive . .	19	104·5	108·5

The factor 5·5 is purely an empirical figure depending upon the method of experiment, the nature and quantity of solvent used, etc. The value of the bromine thermal value is thus relative, not absolute, and each investigator will find it necessary to determine his own factor.[61] It is interesting to compare this method with the Maumené test described below (see p. 52).

Since the rise in temperature in these experiments is a function of the specific heat of the oil and its diluents, as well as of the heat capacity of the apparatus, it is interesting to inquire if a closer agreement would not be obtained between the calculated and observed iodine values if the actual heat evolution, expressed as calories per gram of oil, were determined instead of the rise in temperature. This has been done by a few investigators and the following figures, given by Marden,[62] are interesting:—

Oil.	Heat of Bromination.	Heat of Bromination × 0·846.	Observed iodine value.
Raw linseed	206·0	174·2	172·5
Boiled linseed	204·6	173·0	169·0
Chinese wood	150·0	127·0	156·0
Maize	146·2	123·8	123·1
Rape	120·8	102·2	105·8
Cotton-seed	117·0	99·0	101·7
Castor	104·1	88·1	88·8
Olive	100·7	85·2	84·0

The term **heat of bromination** is preferably reserved for use in the above manner, to express the number of calories of heat evolved per gram of oil, in order to avoid confusion with the bromine thermal value, which expresses merely a rise in temperature (see p. 42). It will be observed that, save in the case of Chinese wood oil, the agreement between the observed and calculated iodine values is reasonably close, but not strikingly superior to that obtained from the bromine thermal values.

LINSEED OIL AND OZONE.

Linseed oil, like its constituent organic acids, readily absorbs ozone at low temperatures, the observed increase in weight per 100 grams of oil being termed the **ozone number** (see p. 18). Since a molecule of ozone is added to each double bond it was to be expected that a close connection would exist between the ozone number and the iodine value. That such is actually the case has been clearly demonstrated by Fenaroli,[31] who gives the following data:—

Oil.	Iodine value.	Ozone No. calculated from $I_2=O_3$.	Ozone No. found.
Olive . .	83·8	15·9	15·8, 16·3
Castor . .	86·4	16·3	16·1, 16·3
Maize . .	114·1	21·6	21·1, 22·1
Linseed . .	176·8	33·5	33·4, 34·6

THE OXIDATION OF LINSEED OIL.

When exposed to the air linseed oil gradually absorbs oxygen, ultimately yielding an elastic, solid mass known as **linoxyn**. It is on account of this peculiarity that linseed oil finds extensive application in the paint trade and in linoleum manufacture.

If the oil is poured on to cotton wool and allowed to oxidise considerable heat is set free which may even lead to conflagration.[32] When, however, the oil is spread in thin films over some relatively non-porous material, as in painting, the heat of oxidation is so widely distributed that no appreciable rise in temperature occurs. Under these conditions a study of the change in weight of the oil film during oxidation is both interesting and instructive. The experiment may be carried out by weighing a glass plate, coated with a thin film of the oil, and exposing it, shielded from dust by a large glass cover, to the air in a room of uniform temperature. The weight of oil should range from 0·1 to 0·15 gram per 100 sq. cm.,[33] for should it exceed this amount the results are untrustworthy, since the outer skin of the film oxidises and sets whilst the under portions remain still liquid. Thinner films than the above yield precisely the same results;[34] but it is not advisable to employ them too thin, for even under the most favourable conditions (say 0·15 gram per 100 sq. cm.) the weight of the glass plate is very great compared with that of the oil, and further reduction of the oil greatly increases the percentage error of weighing. If weighings are made about every ten hours and the alterations in weight plotted in the form of a weight-time curve, a line of the form ABCD in the accompanying diagram is obtained. At first there is a period of induction during which the oil undergoes no appreciable alteration (*i.e.* AB). A rapid increase in weight is now observed rising to a maximum (C in the figure) after which the oil very slowly loses in weight. Usually the oil "sets" or "dries" at a point practically midway between B and C.

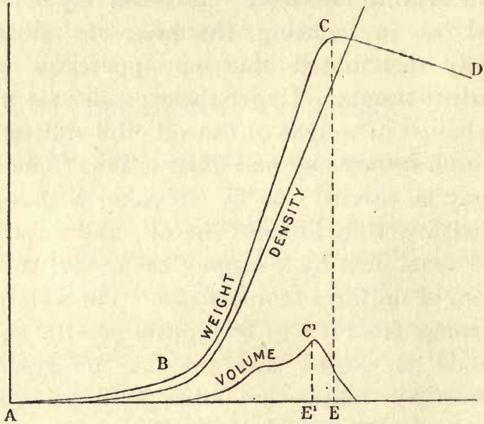


Fig. 1.—Behaviour of linseed oil during drying.

The percentage increase in weight at the point C is frequently termed the **oxygen figure**, but for reasons which will be given shortly it would be more correct to term it the **apparent oxygen figure**. The numerical values obtained for this figure show considerable variation, namely from 13 per cent.[35] to 25·6 per cent.,[36] the usual amount being about 18 per cent.[37] The figures obtained with different oils in this way have frequently been used as a basis of comparison of the drying powers of the oils concerned. If the tests are carried out at the same time and under precisely similar conditions the results may be useful within certain limits. But the method is tedious, and other more suitable ones can be employed to greater advantage.[38]

When a thick layer of linseed oil is allowed to set it invariably crinkles, and this is one reason why painters prefer to give two coats of paint of reasonable thickness rather than one coat of great thickness. The crinkling suggests that a change in volume takes place when linseed oil sets, and this is borne out by the results in the following table:[1]—

Oil used : Best Calcutta raw linseed.
Temperature : approximately 15° C.

Condition of oil.	Increase in weight. Per cent.	Density at 15° C.	Increase in density. Per cent.	Increase in volume. Per cent.
Liquid	0	0·93179	0	0
Do.	2·08	0·94850	1·8	0·28
Do.	5·83	0·97696	4·8	0·87
Thick, frothy liquid .	9·66	1·00123	7·4	2·06
Tacky	14·14	1·0424	11·9	2·0
Just set . . .	17·34	1·0582	13·6	3·3
Solid linoxyn . .	17·90	1·0656	14·3	3·1
Do. . .	18·57	1·0902	17·0	1·35
Do. (3 months old)	10·3	1·1054	18·6	−7

These results are shown diagrammatically in the figure on p. 46. It will be observed that the density of the oil steadily increases, whilst the volume increases to a maximum and then slowly decreases, until after three months a contraction of 7 per cent. has taken place.

Sabin[40] mentions that a raw oil film exposed to the air for eight months yielded linoxyn of density 1·098, the total gain in weight of the oil being not more than 2 per cent. No statement is made of the density of the oil, but assuming it to have the mean value of 0·932, it is easy to calculate that the contraction in volume amounted to 13·4 per cent. This affords a simple explanation of the cracking of paint surfaces,[41] which is such a common feature of old paintwork whether artistic or industrial.

The statement has been made (*vide supra*) that the increase in the weight of the oil gives only the apparent oxygen absorption. The *real* absorption is usually considerably greater, for whilst oxygen is being absorbed, volatile decomposition products are being evolved. Hence the observed increase in weight is less than the total oxygen absorption by the weight of volatile vapours. This is well illustrated by the following figures:[42]—

Time (days).	Percentage increase in weight of oil.	Percentage weight of water and volatile bodies evolved.	Total weight of oxygen taken up by 100 grams of oil.
14	1·07	2·69	3·76
24	1·66	3·88	5·54
33	2·11	4·56	6·67
45	7·97	9·54	17·51
54	9·35	11·52	20·87
58	9·74	12·88	22·62
68	8·96	15·81	24·77

These results are shown graphically in Fig. 2. The point C, representing as before the maximum increase in weight of the oil, is the point at which the weight of oxygen retained is exactly equal to the weight of vapours lost. The true or real oxygen figure (F E) is more than double the apparent figure (C E) in this particular series of experiments. Although Mulder[43] drew attention to it in 1867, and even examined the volatile products evolved, this important fact has been repeatedly overlooked by investigators during more recent years.

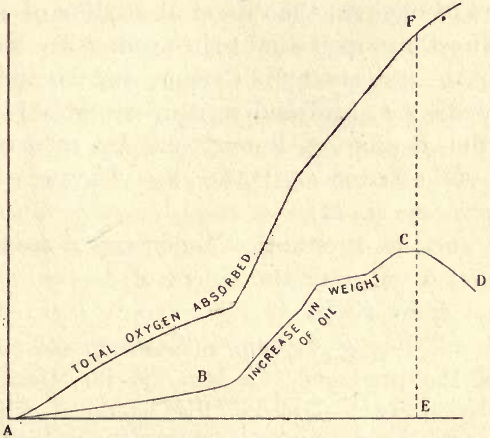


Fig. 2.—Absorption of oxygen by linseed oil.

Now it will be evident that any factor that can assist in the decomposition of the oil will shift the point C to the left; in other words the apparent oxygen value will fall. Sunlight, heat, and the presence of inert pigments,[44] such as barytes or silica, will effect this. Since the alteration in volume during setting is a function of the increase in weight of the oil, it would thus appear impossible to determine by calculation beforehand either figure for any special case.

Both sunlight[45] and heat assist in the setting of the oil, and Fokin,[46] who has carefully studied the kinetics of the oxidation of linseed oil, shows that the rate of setting follows Spring's Rule, in that it is doubled for each ten degrees rise in temperature. The rate of setting is influenced by the pressure of oxygen, the rate of absorption of the gas being directly proportional to its pressure.[46] Moisture retards the setting.[46, 47] Certain metals and their compounds, *e.g.*, lead and manganese, greatly accelerate the drying of linseed oil by reducing the period of induction (A B, fig. 1). They are known as **driers** (see p. 71).

The Volatile Products.—Many experiments have been carried out with the object of determining the chemical composition of the vapours evolved from linseed oil during drying. Water constitutes the bulk of the products. Carbon dioxide, formic and acetic acids were detected by Mulder[48] who also obtained traces of acrylic acid, indicating, presumably, the presence of acrolein in the vapours. In more recent years other aldehydes, such as butyric,[49] have been found, together with minute quantities of carbon monoxide.[50] Although the last-named is an exceedingly poisonous gas, it is probably not evolved in sufficient quantities to prove toxic, but the aldehydic vapours are undoubtedly toxic if inhaled too freely. They are, no doubt, also bactericidal, and this affords an explanation for the good sanitary effect of repainting buildings.

Rancidity. — It is well known that oils upon exposure to air tend to become rancid. Although light accelerates the change, oils may become rancid even in the dark[52]; but in the complete absence of light, air, and moisture, oils may remain unchanged for indefinite periods. The changes involved in rancidity are obscure, but Lewkowitsch,[53] who has ably summarised most of the known facts bearing on the point, concludes that the primary cause of rancidity is the formation of free organic acids by the action of moisture in the presence of soluble ferments, which act as catalysers or accelerators. The free fatty acids are next acted on by oxygen[51] in the air, yielding decomposition products which produce the effect of rancidity.

LINSEED OIL AND SULPHUR.

At ordinary temperatures sulphur has no action on linseed oil, but when the two are heated together the former is absorbed yielding a dark coloured, solid body somewhat resembling rubber in plasticity. It finds application in commerce as a rubber substitute.

Sulphur dioxide has long been known to exert a bleaching action on linseed and other oils,[54] but apparently it is not used for that purpose commercially. The sulphur dioxide is oxidised during the bleaching to sulphuric acid,[55] and after prolonged action the linseed oil is converted into a black solid mass.[56]

Sulphuric Acid.—Mention has already been made of the fact that small quantities of sulphuric acid are used in the commercial purification of linseed oil (see p. 8). The action of the acid is influenced both by its concentration and by the amount of oil with which it is mixed. Thus, with excess of concentrated acid the oil becomes dark in colour, sulphur dioxide and formic acid being evolved.[57]

Maumené[58] observed that drying oils evolve more heat as measured by rise in temperature, than do non-drying oils when mixed with concentrated sulphuric acid, and proposed this as a simple and useful test for their purity. It is the relative, rather than the absolute values of such results that are useful (see p. 43), and it is essential that the tests with different samples of oil be carried out under precisely similar conditions.

Oil.	Iodine value.	Maumené figure, °C.	I. val. / Maumené.
Linseed . .	174·2	124·0	1·40
Do. . .	186·7	133·4	1·40
Poppy-seed . .	135·0	88·4	1·53
Cotton-seed . .	109·0	71·0	1·53
Olive . . .	85·0	46·5	1·82
Do. . . .	81·5	44·0	1·85

Archbutt[59] recommends the addition of 10 c.c. of sulphuric acid of 97 per cent. strength under rapid stirring to 50 grams of oil contained in a beaker surrounded with cotton wool. In the accompanying table are given the Maumené figures of a few of the more common oils,[60] and it will be observed that some connection exists between them and the iodine values. Since sulphuric acid destroys the oil, the heat of reaction can hardly be expected to yield perfectly comparable results.

The connection, however, is sufficiently close to be interesting.

SECTION V.

THE CHEMISTRY OF LINSEED OIL AND LINOXYN.

IN common with most vegetable oils, that from linseed is a mixture of triglycerides of organic acids. The constitution and properties of these acids have already been studied in detail. It remains, therefore, for us to indicate how these acids were first detected, and in what proportions they are believed to exist in ordinary raw linseed oil.

The Qualitative Composition of Linseed Oil.—Sacc[1] appears to have been the first investigator to show that linoleic acid, the essential constituent of linseed oil, is different from oleic acid, the predominating organic acid of olive oil. Thirteen years later, namely in 1857, Schüler[2] arrived at the empirical formula $C_{16}H_{28}O_2$ for **linoleic acid**, attributing to it the same number of carbon atoms as palmitic acid, the formula for which he gave as $C_{16}H_{32}O_2$. The formula $C_{16}H_{28}O_2$ was subsequently supported by Mulder[3] in the course of his extensive researches on linseed oil.

Mulder also essayed to determine what other acids besides linoleic are present in the oil. To this end a clear solution of freshly pressed oil was saponified with potassium hydroxide, and the organic acids precipitated as lead soap by addition of lead acetate.

After washing and drying the precipitate the free acids were liberated by dilute sulphuric acid, dissolved in alcohol, and the solution thus obtained allowed to slowly evaporate.

Two practically equal lots of crystals were obtained melting at 62° and 53·5° C. respectively, and constituting about 10 per cent. of the acids taken. The remaining 90 per cent. was left as a non-crystalline buttery mass when all the alcohol had evaporated.

The crystals proved to be those of **palmitic**[4] and **myristic acids**, the correct melting-points of which, in the pure state, are 62·6° and 53·8° C. (see p. 27). No **stearic acid** was found although its presence in linseed oil had been postulated by Unverdorben,[4] and has since been confirmed by Haller[5] and Morrell.[6] The former investigator[5] has also demonstrated the presence of **arachidic** acid in linseed oil.

It now remained to resolve the buttery mass into its constituents, a problem which Mulder attacked indirectly as follows:—

When linseed oil is spread in a thin film on a glass plate it absorbs oxygen from the air and sets to an insoluble, elastic mass known as linoxyn. It is chiefly the glyceride of linoleic acid, however, that has undergone oxidation, the other glycerides being practically unaltered.[30] The unaltered glycerides can be dissolved out of the linoxyn by treatment with ether. Mulder found that 20 per cent. was extractable in this way, indicating that 80 per cent. consists of linolein. Of the soluble portion, as has already been seen, palmitic and myristic glycerides were estimated to constitute 25 per cent.

each, or 5 per cent. each of the original oil.[7] This leaves a balance of 50 per cent. of the soluble extract, or 10 per cent. of the original oil, which consists of the glyceride of **oleic acid**, namely olein.

Here the matter rested for nearly twenty years. In 1886 Peters[8] showed that the analyses of linoleic acid as given by Schüler and supported by Mulder were not quite correct, and that the molecule contains eighteen atoms of carbon, not sixteen. On reduction with hydriodic acid in the presence of phosphorus linoleic acid yielded stearic acid, $C_{17}H_{35}.COOH$, and this result was shortly afterwards confirmed by Dieff and Reformatzki.[9] Peters therefore suggested the formula $C_{18}H_{32}O_2$ or $C_{17}H_{31}.COOH$ for linoleic acid.

An important advance was made by Hazura[10] the following year. The barium salt of linoleic acid was prepared and the iodine value of the free acid found to be 199·2, that calculated for $C_{18}H_{32}O_2$ being only 181·4 on the assumption of two ethylene bonds in the molecule. This suggested that linoleic acid is a mixture of $C_{18}H_{32}O_2$ and some acid of higher iodine value. The latter might conceivably be a lower member of the same series of unsaturated acids, namely $C_nH_{2n-4}O_2$, where n is less than 18; but this is negatived by the analysis of Peters referred to above, indicating that for linoleic acid the mean value of n is just 18.

Hazura therefore concluded that the new acid contained three ethylene groups, and belonged to a new series of acids of general formula $C_nH_{2n-6}O_2$. He termed it **linolenic acid**, $C_{18}H_{30}O_2$, and to avoid confusion gave the name **linolic acid** to $C_{18}H_{32}O_2$.

These formulæ were confirmed in two ways, namely by bromination and oxidation. Linolic acid yields a tetrabromide, $C_{18}H_{32}O_2Br_4$, with bromine, and, upon oxidation with alkaline permanganate, sativic acid $C_{18}H_{32}O_2(OH)_4$. Linolenic acid, on the other hand, was found to yield a hexabromide, $C_{18}H_{30}O_2Br_6$, and two isomeric hexahydroxystearic acids, $C_{18}H_{30}O_2(OH)_6$, which Hazura termed linusic and iso-linusic acid respectively.[11] Hazura concluded that iso-linusic acid indicated the presence of iso-linolenic acid in linseed oil, but no attempt was made to isolate the latter. As to whether or not isomerides of linolenic acid do occur in linseed is still a matter of doubt (see p. 23). In the sequel the term linolenic acid will alone be used, and will be considered as referring to the normal acid and any of its isomerides should such at some later date be proved definitely to occur in linseed oil.

From the foregoing it is evident that linseed oil consists of a mixture of triglycerides containing the following acids:—

1. *Saturated acids*—

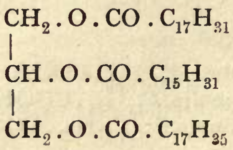
Stearic, $C_{17}H_{35}.COOH$
Palmitic, $C_{15}H_{31}.COOH$
Arachidic, $C_{19}H_{39}.COOH$
and possibly Myristic, $C_{13}H_{27}.COOH$ (see p. 27).

2. *Unsaturated acids*—

Oleic, $C_{17}H_{33}.COOH$
Linolic, $C_{17}H_{31}.COOH$
Linolenic, $C_{17}H_{29}.COOH$.

A small quantity of unsaponifiable matter is also invariably present; it should not exceed 1·5 per cent.,[15] and is usually less than 1 per cent. (see p. 63).

The Nature of the Glycerides in Linseed Oil.—Although it is frequently convenient to assume, for purposes of calculation, that the different acids are present in linseed oil as simple triglycerides, a considerable weight of evidence has gradually been accumulated in favour of the view that mixed triglycerides occur in considerable quantity, if not indeed almost exclusively (see p. 12). Hehner and Mitchell[12] appear to have been the first to draw attention to this possibility as the result of their analyses of the precipitated bromides obtained by adding bromine to ethereal solutions of linseed oil. Hexabromolinolenic glyceride would contain 62·28 per cent. of bromine, whilst tetrabromolinolic glyceride would contain only 52·23 per cent. In practice the amount was found to vary from 55·55 to 56·38 per cent., which suggests that the precipitates consist of brominated mixed glycerides. This suggestion receives support from the work of Morrell[13] and Schlicht.[14] The last-named investigator exposed a sample of La Plata oil to −8° to −10° C. and examined the small fraction of solid fat that separated out. He found it to be mainly linolo-palmito-stearin.



$$\begin{array}{l} \mathrm{CH_2\,.\,O\,.\,CO\,.\,C_{17}H_{31}} \\ | \\ \mathrm{CH\,.\,O\,.\,CO\,.\,C_{15}H_{31}} \\ | \\ \mathrm{CH_2\,.\,O\,.\,CO\,.\,C_{17}H_{35}} \end{array}$$

Traces of other mixed glycerides were also obtained, these being, in all probability, di-oleo-stearin, linolo-di-stearin, and oleo-linolo-palmitin.

It will be evident that with the seven acids which linseed oil may contain, a very considerable number of mixed triglycerides is possible.

The Relative Proportions of the Constituents in Linseed Oil.—It now remains for us to determine the proportions in which the various constituents of linseed oil occur. This is a problem of no small difficulty, and the results are still a matter of dispute. It will be remembered that the general properties of linseed oil exhibit considerable variation according to the source of the seed and the manner in which the oil is expressed. A corresponding variation in the composition of the oil may therefore be reasonably anticipated, and the most we can hope to do is to arrive at either a mean result or a statement of the maximum and minimum amounts of each constituent normally found in pure, unadulterated raw linseed oil.

The problem may be attacked in two ways, namely, either by treatment of the oil itself, or by saponification of the latter and detailed examination of the free organic acids. Both of these methods have been attempted.

As has already been mentioned, Mulder concluded that the free acids of linseed oil contained the following mixture :—

Saturated acids	Palmitic . .	5 per cent.
	Myristic . .	5 „
Unsaturated acids	Oleic . .	10 „
	Linoleic . .	80 „

Allowing 1 per cent. of unsaponifiable matter in the original oil, it is easy to calculate the composition of the last-named to have been as follows: [16]—

Unsaponifiable matter	1·0	per cent.
Saturated acids	9·4	„
Oleic acid	9·5	„
Linoleic acid	75·8	„
Glyceryl radicle (C_3H_5)	4·3	„
Total	100·0	

Considering the difficulties under which Mulder laboured, it must be acknowledged that this result is surprisingly near to the mean composition arrived at in more recent years. By linoleic acid we understand a mixture of linolic and linolenic acids, since the composite character of the linoleic acid was unknown to Mulder, being demonstrated by Hazura and his co-workers some twenty years later[10] (see p. 56). Hazura[11] sought to determine the relative proportions of the unsaturated acids in linseed oil by brominating them in the free state. The oil was saponified and the acids liberated. Bromination of 50 grams of these yielded 20 grams of linolenic hexabromide, equivalent to 7·5 grams or 15 per cent. of the free acid. Since on oxidation of the unsaturated acids from linseed oil only small quantities of dihydroxystearic acid were obtained, namely 1·2 per cent., it was assumed that only a small percentage of oleic acid could be present, the amount being taken in round figures as 5 per cent. This leaves a balance of 80 per cent. of linolic and iso-linolenic acids. Of this 15 per cent. was taken to be linolic acid.[17] To sum up, the composition of the unsaturated acids of linseed oil was thus found to be—

Oleic acid	5	per cent.
Linolic acid	15	„
Linolenic acid	15	„
Iso-linolenic acid	65	„
Total	100	„

Assuming the presence in the original oil of 1 per cent. unsaponifiable matter, and 9 per cent. of glycerides of saturated organic acids, the composition of the original oil would be[16]—

Unsaponifiable matter	1·0	per cent.
Saturated organic acids	8·6	„
Oleic acid	4·3	„
Linolic acid	12·9	„
Linolenic acid[19]	68·9	„
Glyceryl radicle (C_3H_5)	4·3	„
Total	100·0	„

A useful check on the probability of such figures being correct is afforded by the iodine value (see p. 37). The value for an oil of the composition given above is readily calculable from the following data:—

The unsaponifiable matter, organic acids, and glyceryl radicle do not absorb iodine. The theoretical iodine values of oleic, linolic, and linolenic acids are 90·1, 181·4, and 273·8 respectively.

Whence—

		Iodine value.
4·3 per cent.	oleic acid	3·87
12·9 „	linolic acid	23·40
68·9 „	linolenic acid	188·65
	Total	215·92

The iodine value is thus seen to be 215·9, which is far higher than the highest figure ever obtained for the oil (see p. 40). This implies that the percentage of linolenic acid is too great; for even if the linolic acid were reduced to nil, being entirely replaced by oleic acid, the iodine value would only fall to 204, whereas the usual value lies between 170 and 180.

In 1903 Fahrion,[18] after a careful consideration of all the available data, concluded that the composition of linseed oil is, on an average, represented as follows:—

	Per cent.	Calculated iodine value.
Unsaponifiable matter	0·8	...
Saturated organic acids	8·0	...
Oleic acid	17·5	15·8
Linolic acid	26·0	47·1
Linolenic acid[19]	43·5	119·1
Glyceryl radicle	4·2	...
	100·0	182·0

Seven years later these figures were modified by Fahrion[20] as follows:—

	Per cent.	Calculated iodine value.
Unsaponifiable matter	0·6	...
Saturated organic acids	9·3	...
Oleic acid	17·5	15·8
Linolic acid	30·0	54·4
Linolenic acid[19]	38·0	104·0
Glyceryl radicle	4·6	...
	100·0	174·2

With reference to these later figures it will be observed that the percentage of saturated organic acids lies practically midway between the 5 per cent. suggested by Fokin[21] and the maximum of 15 per cent. saturated organic acid glycerides (corresponding to 13·3 per cent. of free acid) as given by Benedikt and Ulzer.[20] It is probably a fair average. The value for oleic acid is high, and necessitates a fairly high percentage of linolenic acid in order to afford the correct iodine value.

If the oleic acid were reduced to 5 per cent., the same iodine value would be obtained with 56·4 per cent. of linolic acid and 24·6 per cent. of linolenic acid. Thus—

	Iodine value.
5 per cent. oleic acid	4·5
56·4 „ linolic acid	102·3
24·6 „ linolenic acid[19]	67·4
	174·2

This is more in harmony with the conclusions of Erdmann and Bedford,[22] namely, that linseed oil contains not more than about 20 to 25 per cent.

of linolenic acid, and of Fokin,[21] who gives 22 to 25 per cent.

The evidence, though admittedly conflicting, would appear to suggest that the composition of linseed oil of iodine value ranging from 170 to 180 lies between the following approximations:—

Constituents.	Per cent.	I. value.	Per cent.	I. value.
Unsaponifiable matter Saturated organic acids	10	0	10	0
Oleic acid . . .	5	4·5	5	4·5
Linolic acid . .	59·1	107·2	48·3	87·9
Linolenic acid . .	21·3	58·3	32·1	87·6
Glyceryl radicle . .	4·6	0	4·6	0
	100·0	170·0	100·0	180·0

Further research on this interesting subject is eminently desirable.

The Constitution of Linoxyn.—The tough elastic solid obtained by oxidation of linseed oil is known as linoxyn (see p. 44). Owing to the difficulty of effecting its solution without decomposition, however, its constitution is not yet known although many useful suggestions have been offered from time to time.

That linoxyn contains glycerol was first demonstrated by Bauer and Hazura[23] who saponified it, and after removing the acids estimated the glycerol in the residue as 5 per cent. of the original weight of linoxyn taken. This completely disposed of Mulder's view that linoxyn consists only of oxidation products of the organic acids, the glycerol having been oxidised away to volatile products.

It was concluded from this and other experiments that oxidation proceeds mainly with linolenic and linolic acids and not with oleic and the saturated organic acids; and in as much as linolenic acid exhibits the highest degree of unsaturation, and has the highest iodine value, the drying power of an oil rises in proportion to the amount of this acid present, and hence with the iodine value.[11]

Finally, Bauer and Hazura suggested that the oxidation of the glycerides takes place in an exactly similar manner to that of the free acids; in other words, that the glycerol exerts practically no influence upon the *modus operandi* of the reactions. This assumption has received substantial support from the work of Fahrion[24] in more recent years.

Weger[27] appears to have been the first to suggest that peroxides are formed during the oxidation of linseed oil, and Fahrion concluded that such is almost certainly the case when the free acids from linseed oil are exposed to the air. His method of arriving at this conclusion is interesting. A sample of the free acids, of iodine value 187·4, was oxidised in a current of air, the total gain in weight being 13·1 per cent. The iodine value of the residue was found to be 65·7, equivalent to 74·3 for the original acids. Hence—

$$\frac{\text{Fall in I. value}}{\text{Wt. of Oxygen absorbed}} = \frac{113\cdot 1}{13\cdot 1} = \frac{127 \times 2}{15 \times 2} = \frac{I_2}{O_2} \text{ (approx.).}$$

The above result indicates that for each molecule of oxygen taken up one of iodine ceases to be absorbed.[25] This is in harmony with Engler's [26] theory of autoxidation according to which whole molecules of oxygen, rather than single atoms, are taken up by substances during spontaneous oxidation, peroxides being formed. Thus, if L represents the molecule of linseed oil, and n the number of molecules of oxygen absorbed,

$$L + nO_2 = L(O_2)_n.$$

In linseed oil we have two acids capable of absorbing oxygen, namely linolenic, with three double bonds and linolic with two. Linolenin has nine double bonds and linolin six, so that a molecule of the former should be capable of absorbing nine molecules of oxygen—

$$\underset{\text{Linolenin.}}{C_{57}H_{92}O_6} + 9O_2 = \underset{\substack{\text{non-oxylinolenic}\\\text{triglyceride.}}}{C_{57}H_{92}O_{24}}$$

and linolin, six—

$$\underset{\text{Linolin.}}{C_{57}H_{98}O_6} + 6O_2 = \underset{\substack{\text{hexaoxylinolic}\\\text{triglyceride.}}}{C_{57}H_{98}O_{18}}$$

Linoxyn will thus consist of these two oxidised bodies together with the small quantities of unchanged olein and glycerides of saturated organic acids originally present in the oil. Now the ratio of carbon to hydrogen in these two oxidised substances is as follows:—

In $C_{57}H_{92}O_{24}$ $C : H = 7{\cdot}4 : 1$

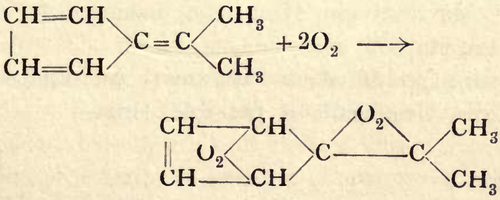
$C_{57}H_{98}O_{18}$ $C : H = 7{\cdot}0 : 1$

Mulder found, upon analysing linoxyn, the following ratio:—

$$C : H = 7{\cdot}03 : 1$$

as a mean of three analyses, that is, a value closely approaching the hexaoxylinolic triglyceride. This is in harmony with the conclusion of Fokin[21] that linolic and not linolenic acid is the main constituent of linseed oil. On the other hand, as Fahrion[28] is careful to point out, this may be due to the presence of unoxidised portions, or to the fact that partial oxidation only has taken place. The former state might well be due to polymerisation[28] of some of the unoxidised molecules to a resistant polymeride, whilst the latter may be explained on the assumption that oxidation takes place in stages.

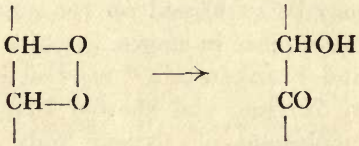
Engler and Frankenstein[29] studied the oxidation of dimethyl fulvine, and showed that it combines with two molecules of oxygen only, although it possesses three double bonds. The exact composition of the oxidation product is uncertain, but the following scheme is suggested:—



Fahrion[24] is of the opinion that an analogous reaction obtains with linolenic and linolic acids.

Oleic acid, with one double bond, absorbs no oxygen; linolic, with two, absorbs one molecule; whilst linolenic, with three, like dimethyl fulvine, absorbs two molecules of oxygen. The primary oxidation products are thus peroxylinolic acid, $C_{17}H_{31}O_2 . COOH$, and diperoxylinolenic acid, $C_{17}H_{29}(O_2)_2 . COOH$, respectively. The glycerides of these acids will behave similarly, since the glycerine appears to exert no influence upon the manner in which the acids attached to it are oxidised (*vide supra*).

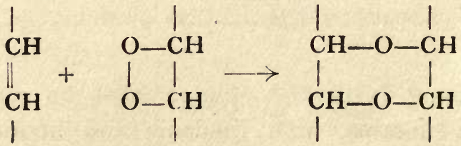
These peroxy acid radicles are capable of undergoing several changes. Thus intramolecular rearrangement may take place as follows:—



$$\begin{array}{l} | \\ \mathrm{CH{-}O} \\ |\quad\;\; | \\ \mathrm{CH{-}O} \\ | \end{array} \longrightarrow \begin{array}{l} | \\ \mathrm{CHOH} \\ | \\ \mathrm{CO} \\ | \end{array}$$

a hydroxyketoxy acid radicle resulting in the case of linolin, and a dihydroxy-diketoxy radicle with linolenin. Such substances readily lose water yielding[30] derivatives after the nature of lactones, lactides, etc.

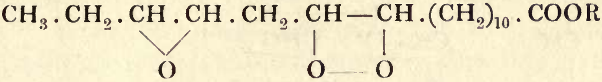
Again, combination between an oxidised and unoxidised molecule is possible, thus—



$$\begin{array}{l} | \\ \mathrm{CH} \\ \| \\ \mathrm{CH} \\ | \end{array} + \begin{array}{r} | \\ \mathrm{O{-}CH} \\ |\quad\;\; | \\ \mathrm{O{-}CH} \\ | \end{array} \longrightarrow \begin{array}{l} |\qquad\qquad\;\; | \\ \mathrm{CH{-}O{-}CH} \\ |\qquad\qquad\;\; | \\ \mathrm{CH{-}O{-}CH} \\ |\qquad\qquad\;\; | \end{array}$$

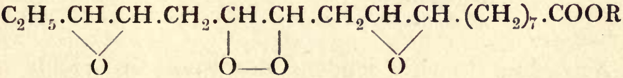
It will thus be seen that many possibilities arise. Fahrion therefore concludes that linoxyn consists of peroxylinolic and diperoxylinolenic acids, partly free, partly bound to glycerine, and partly converted to ketoxy acids. In addition to these linoxyn also contains unoxidised olein and glycerides of the saturated organic acids.

Orloff,[31] on the other hand, suggests that linolic * and linolenic glycerides yield, upon oxidation, the following substances respectively :—



$$\mathrm{CH_3.CH_2.\underbrace{CH.CH}_{O}.CH_2.\underbrace{CH{-}CH}_{O{-}O}.(CH_2)_{10}.COOR}$$

and



$$\mathrm{C_2H_5.\underbrace{CH.CH}_{O}.CH_2.\underbrace{CH.CH}_{O{-}O}.CH_2\underbrace{CH.CH}_{O}.(CH_2)_7.COOR}$$

The views of Salway [32] are particularly interesting in this connection. As has already been mentioned (see p. 26) this investigator shows that, if linolenic acid is regarded as a derivative of hexatriene, a satisfactory explanation is forthcoming for the presence of acrolein and the oxides of carbon among the volatile oxidation products of linseed oil.

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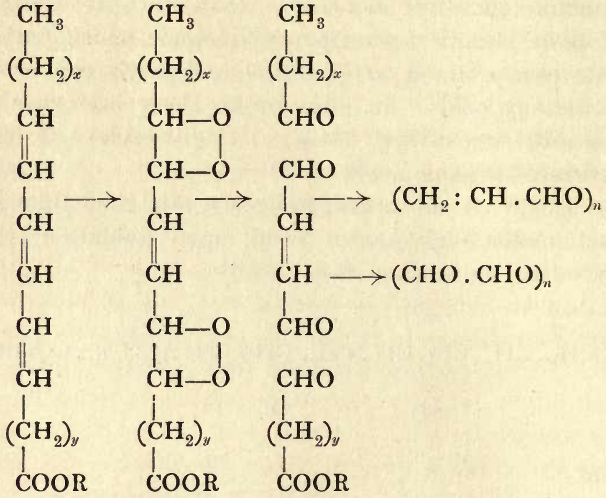
* It will be observed that Orloff does not use Goldsobel's formula for linolic acid (p. 21).

Thus—



Linolenin. Dioxygenide or diperoxide of linolenin.

According to this scheme the linolenin yields a dioxygenide, the central double bond remaining unaffected on account of its greater stability. The oxygenide wholly or partially decomposes with the formation of aldehydes, the greater proportion of which then polymerise yielding, with the unchanged oil—namely olein and saturated organic acid glycerides—the substance called linoxyn. A small quantity of free acrolein, carbon monoxide and carbon dioxide would also be evolved in accordance with the scheme shown on p. 26.

The author modestly admits[32] that "whilst there is considerable evidence in favour of this theory . . .

further research is necessary before its validity can be considered established."

Other suggestions have been made,[34] but the above will suffice to illustrate the more important lines along which the subject has been attacked as well as to show the extreme difficulty of the whole problem.

Superoxidised Linseed Oil.—Does oxidation cease when linoxyn has been formed? The answer is in the negative. Reid[35] mentions that if a surface of pure linoxyn is exposed to the air for several years it gradually softens, ultimately becoming a fluid mass soluble in alcohol. This he terms "superoxidised oil." What its constitution may be is at present unknown. Reid points out, however, that this liquefaction accounts for the stains in old printed books, the linoxyn of the printers' ink "runs" during superoxidation, and is absorbed by the paper.

THE ACTION OF DRIERS ON LINSEED OIL.

Ordinary raw linseed oil sets much too slowly for the painter, and in order to hasten the process it is usual to add certain metals or their compounds to the oil. Such additions are known as **siccatives** or **driers**, and if they are suitably chosen and used in the right proportions, an ordinary coat of paint may be made to set in a very few hours.

The Livache Test.—It has long been known that linseed oil sets considerably more rapidly when spread on a sheet of lead than on a plate of glass. Livache[36] suggested a method of testing oils by making use of this power possessed by lead of accelerating their oxidation when exposed to air. Finely divided lead is first prepared by precipitation from a lead salt with zinc, washing successively with water, alcohol, and ether, and finally drying *in vacuo*. About 1 gram of the metal is carefully weighed in a clock glass and spread out into a thin layer. A few drops of oil, weighing *in toto* not more than about 0·7 gram, are allowed to fall on different parts of the glass, particular care being taken that the drops do not run together and coalesce. The glass is now allowed to stand exposed to air and diffused daylight, but shielded from dust, and at regular intervals is weighed. Whilst the drying oils show a marked increase in weight within twenty-four hours, non-drying oils do not alter appreciably within four or five days. Livache also tested the organic acids from a number of common oils, but found that they absorbed oxygen much more slowly; those obtained from the drying oils, however, generally absorbed oxygen at a greater rate than the others.

Some of the results obtained by Livache are as follows:—

Oil.	Percentage increase in weight of oil after two days.	Percentage increase in weight of free organic acids after eight months.
Linseed . .	14·3	11
Walnut . .	7·9	6
Poppy . .	6·8	3·7
Cotton-seed .	5·9	0·8
Beechnut. .	4·3	2·6
Colza . .	0	2·6
Olive . .	0	0·7

Numerous modifications of the Livache test have been suggested from time to time,[37] and for comparative purposes no doubt the test is not altogether without value. Livache carried out other tests in a similar manner with tin and copper, but found the activity of these metals to be relatively feeble. Fokin,[38] who has studied the problem in detail, arranges the metals that assist the oxidation of linseed oil in the following order, the most powerful catalysers being placed on the left:—

Co, Mn, Cr, Ni, Fe, Pt, Pd, Pb, Ca, Ba, Bi, Hg, U, Cu, Zn.

He also shows that the velocity of the reaction increases with the cube root of the concentration of the catalyser.

Not only may finely divided metals be used as driers, but their oxides and salts, particularly certain organic salts, are now largely employed. The most important inorganic driers are red lead; litharge; lead borate; oxide, borate, and sulphate of manganese. The more important semi-organic driers are the rosinates and linoleates of lead, cobalt, and manganese,[39] lead acetate and manganese oxalate.

Chemical Action of Driers.—The question now arises as to the manner in which the driers act. Mulder concluded that the metals serve as oxygen carriers, and in support of this it will be observed that the metals which act most vigorously as catalysers (see Fokin's list above) are those which readily form higher and lower oxides.

Now if the metals (or their compounds) really act in no other way than as oxygen carriers or catalysers it will be evident that the amount of oxygen absorbed by a given sample of oil during setting may be expected to remain the same no matter what amount of catalyser may be present. Unfortunately, however, we have no data on this point. It is true that Lippert[40] found that the maximum increase in weight of linseed oils containing varying quantities of lead oxide as drier gradually rose as the percentage of oxide fell. Thus—

PbO Per cent.	Maximum increase in weight Per cent.
6·8	12·3
2·5	12·7
1·1	13·9
0·34	14·5

But, as has already been pointed out, the maximum increase in weight only gives the apparent and not the real oxygen absorption (see p. 46) so that these figures do not help us much.[41] The balance of the scanty evidence in our possession points to the assumption that Mulder's theory is correct, namely, that the siccatives act mainly if not entirely as pure oxygen carriers or catalysers.

SECTION VI.

Polymerised and Oxidised Oils.

Linseed oil is frequently thickened for commercial purposes by heating either in the relative absence of air or else whilst a rapid stream of air is passed through it. In the former case very little oxidation takes place, the products being termed **polymerised** or **litho oils**; whilst in the latter case considerable oxidation is effected, **boiled** or **blown oils** resulting.

Polymerisation of Linseed Oil.

When heated in the absence of air linseed oil gradually thickens and its iodine value falls, as does also its yield of hexabromides. This is well illustrated by the following figures given by Ingle,[1] who examined samples of oil that had been kept for varying lengths of time at 195°-200° C. :—

Duration of Heating. Hours.	**Density.**	**Iodine value.**	**Hexabromides.**
0	0·9315	179·5	35·3
2	0·9350	175·5	30·7
4	0·9383	170	27·4
6	0·9148	165	26·2
11	0·9501	154	16·0
15·5	0·9583	145	10·5
43	0·9800	121	0·9

Closely similar results are obtained by heating the oil for shorter periods to higher temperatures. A particularly interesting series of experiments was carried out along these lines by Krumbhaar,[2] from which the following data are taken. The oil was heated in a current of carbon dioxide so that the effects of oxidation were entirely excluded from the results.

Temp. °C.	Duration. Hours.	Acid value.	Saponification value.	Viscosity (relative).	Iodine value.	Refractive index 25° C.	Specific gravity 25° C.
...	...	1·1	194·5	1·00	175·0	1·479	0·924
200	20	2·6	193·9	1·13	168·7	1·480	0·926
200	40	3·4	194·8	1·35	160·1	1·482	0·929
260	15	5·8	192·0	2·35	145·6	1·486	0·933
260	30	7·4	191·1	7·96	108·0	1·489	0·946
300	10	17·8	193·1	115·0	120·4	1·492	0·961
300	20	40·0	191·2	(not flow)	76·3	1·496	0·970

The acid value showed a remarkable rise, whilst the saponification number remained fairly constant. Of particular interest are the relative viscosities, the final 40° rise in temperature causing a thickening out of all proportion to the effect produced at 260° C. and below. After twenty hours at 300° C. the oil was so thick that it ceased to run, and its viscosity could not be determined. The refractive index and density rose with the viscosity.

The fall in the iodine value led Fahrion[3] in 1892 to suggest that polymerisation had taken place, and this was confirmed by Fokin[4] who found that by heating linseed oil in a sealed tube to 250°-300° C. a substance of molecular weight approximating to 2000 was obtained. Other investigators have obtained analogous results.[5] The figures in the accompanying table show that polymerisation may be observed at temperatures as low as 200° C., and that it rapidly increases in extent with rise of temperature and with the duration of the heating.[6]

Duration of heating. Hours.	Temperature °C.	Molecular weight.	Coefficient of expansion with rise of temperature.
0	...	740	0·000760
30	200	760	0·000743
36	300	1000	0·000741
42	300	1420	0·000717

It is interesting to note that the coefficient of expansion with rise of temperature shows a steady decrease as the molecular weight rises.

Morrell[5] found that linseed oil, thickened at 260°-280° C., contained two modifications,[7] both of which were soluble in light petroleum but one only in acetone. The properties of these are given in the following table:—

	Original Linseed oil.	Thickened oil.	
		A. Part insoluble in Acetone.	B. Part soluble in Acetone.
Specific gravity (15° C.) .	0·933	0·9763	0·9527
Refractive index . .	1·4831	1·4964	1·4846
Molecular weight . .	805	1788-2517	904-975
Saponification number .	197	190-204	193
Iodine value . . .	185	97-121	92-143
Acid value	0·4	0·2	7·5-8·0

Approximately equal quantities of the two components A and B were present in the oil thickened at 260° C. Part A exhibits every evidence of polymerisation, its density and refractive index being considerably higher than that of the original oil, while its molecular weight is twice or three times as great. The lead and barium salts of these oils were prepared, and from them the free organic acids. It was found that all traces of linolic and linolenic acids had disappeared, and Morrell concludes that linkage changes must have occurred during thickening and anterior to the polymerisation. The probability is that linolenin, or if mixed glycerides are present, those containing linolenic acid, are the first to undergo .polymerisation on account of the higher condition of unsaturation of linolenic acid, and are hence the main source of component A. The remainder, B, will thus be derived largely from the glyceride containing linolic and other more saturated acids. This receives substantial support from the fact that thickened poppy-seed oil closely resembles component B. Now raw poppy-seed oil contains linolic acid but practically no linolenic acid.[5] The inference is clear.

From the foregoing it is evident that the thickening of linseed oil in the absence of oxidation is due to polymerisation, the first stage being the formation of a product insoluble in acetone consisting of polymerised glycerides. The precise constitution of these complexes is at present unknown.

Uses.—Litho oils or *Stand oils*[8] are used in lithographic printing and in the manufacture of printers inks.

BLOWN OILS.

Ordinary boiled or blown oil is obtained by heating raw linseed to about 95° C. in a tank fitted with a closed steam coil. After a couple of hours of this preliminary treatment, which serves to reduce frothing at a later stage, the oil is transferred to a steam-heated boiler, and a current of air blown through, the oil being thoroughly stirred by mechanical agitators during the process. Driers, such as the oxides of lead and manganese, are added in small quantities at a time until about 10 lb. have been consumed per ton of oil.[9]

The oil is now allowed to settle in tanks for several days, the clear liquid being decanted and used for paints, etc., whilst the impure residue, termed "foots," is used for putty.

As obtained in this way boiled oil is a thick liquid of darker colour and greater density than the original raw oil. It readily sets to a glossy coat when exposed in thin films to the air, its rate of setting being considerably greater than that of the pure raw oil, the initial period of induction (A B, fig. 1) being very short. Its apparent oxygen figure (p. 46) is appreciably smaller than that of raw oil. The density of the commercial oil usually ranges from 0·945 to 0·950. It is soluble in turpentine and other similar organic solvents, and is almost completely saponifiable by alcoholic potash.

Actinic Rays.—It is well known that light, particularly the actinic rays, frequently accelerate chemical reactions. The setting of linseed oil is no exception to this, the process taking place far more quickly in sunlight than in the dark.[10] Since the light emitted from a mercury vapour lamp is particularly rich in actinic rays, Genthe[11] suggested that it might be advantageously utilised in the production of blown oils. To this end the oil is run into a tank of 1000 kg. capacity, containing a series of uviol lamps.[12] The oil is warmed to about 80° C. and the lamps started. Air is now blown through, the light from the lamps assisting the absorption of the oxygen, and the heat of the reaction keeping the temperature at the necessary point. The oil increases in weight by about 5 per cent., being also bleached and thickened. When spread in a thin film it rapidly sets to a bright surface, and is recommended for the linoleum industry.[13]

Effect of Oxidation on the Constants of Linseed Oil.—It is instructive to examine the effect of blowing for varying lengths of time on the constants of linseed oil. For this purpose the data published by Procter and Holmes[14] are very suitable, and are as follows:—

Temperature 100° *C.*

Hours. Blown.	Density 15° C.	Refractive index 15° C.	Iodine value. (Hanus.)
0	0·930	1·4817	164·5
4	0·932	1·4820	164
8	0·933	1·4820	158
12	0·934	1·4827	147·5
16	0·940	1·4834	145
20	0·942	1·4840	140·5
24	0·943	1·4840	139·5

It will be observed that the density and refractive index steadily rise whilst the iodine value falls. This is similar to what obtained during the heating of raw oil in the absence of oxidation (see p. 75).

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(*The Abbreviations used are substantially the same as those adopted by the Chemical Society, London.*)

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[34] Rollett, ibid., 1909, **62**, 424.

[35] Salway, Trans. Chem. Soc., 1916, **109**, 138.

[36] Bauer and Hazura, Monatsh., 1888, **9**, 459.

[37] These acids were discovered by this reaction by Hazura who gives the following melting-points: linusic, 203°-205° C.; iso-linusic, 173°-175° C. (Monatsh., 1888, **9**, 180). The argument that two linolenic acids corresponding to these must exist, loses much of its force, however, from the observation of Mangold (Monatsh., 1892, **13**, 326), that from one and the same homogeneous ricinoleic acid, two isomeric oxidation products are obtainable on oxidation with permanganate. There is no apparent reason, therefore, why the same should not be true for linolenic acid.

[38] Erdmann and Raspe, Ber., 1909, **42**, 1334.

[39] See Salway and Kipping, Trans. Chem. Soc., 1909, **95**, 166.

[40] Fremy, Liebig's Annalen, 1840, **36**, 44.

[41] Edmed, Trans. Chem. Soc., 1898, **73**, 627.

[42] See Gmelin, Handbuch der Chemie (Kraut), 1866, vol. vii., pp. 1230-1233.

[43] Haller, Compt. rend., 1908, **146**, 259.

[44] Playfair, Liebig's Annalen, 1841, **37**, 152.

[45] Baczewski, Monatsh., 1896, **17**, 530.

[46] Morrell, J. Soc. Chem. Ind., 1913, **32**, 1091.

SECTION IV.

[1] Friend, Trans. Chem. Soc., 1917, **111**, 162.

[2] Bulletin No. 107, U.S. Department of Agriculture. See J. Ind. Eng. Chem., 1914, **6**, 164.

[3] The terms *specific gravity* and *density* are frequently misapplied. The density is the weight in grams of 1 c.c. of a substance. The specific gravity is the number of times heavier a substance is than an equal volume of water at a given temperature. Since 1 c.c. of water at 4° C. weighs 1 gram, density and specific gravity at this temperature are the same numerically. Specific gravity at, say 15° C., is the ratio of the weights of the substance at 15° C. and an equal volume of water at 15° C., whilst the density at 15° C. is the ratio of the weights of the substance at 15° C. and an equal volume of water at 4° C.

[4] Sheppard, J. Ind. Eng. Chem., 1912, **4**, 14.

[5] Crampton, Amer. Chem. J., 1889, **11**, 232.

[6] Wright (J. Soc. Chem. Ind., 1907, **26**, 513) found $\alpha = 0{\cdot}00069$ for linseed oil; his results are consistently lower than those of Crampton. Crampton did not determine α for linseed oil. Evidently variation occurs in this as in other properties according to the source, etc., of the oil.

[7] Sjollema, Zeitsch. Unters. Nahr. Genussm., 1903, **6**, (14), 631.

[8] Lewkowitsch, Chemical Technology and Analysis of Oils, Fats, and Waxes (MacMillan & Co.), 1913, vol. i., p. 434.

[9] It would be better, for the sake of uniformity with the hydrogen, iodine, ozone, and certain other "values" to adopt 100 grams of oil as the basis rather than 1000 grams.

[10] Morrell (J. Soc. Chem. Ind., 1915, **34**, 105) found that by heating linseed oil to approximately 260° C. in an atmosphere of hydrogen gas "a very slight addition occurred."

[11] Sabatier and Senderens, Ann. Chim. Phys., 1904, (viii.), **4**, 319; Ber., 1911, **44**, 1984.

[12] Skita, Zeitsch. angew. Chem., 1913, **26**, 601; Chem. Zeit., 1914, **38**, 605. But platinum is more sensitive to poisons (Wieland, Ber., 1912, **45**, 2615).

[13] Paal and Roth, Ber., 1908, **41**, 2283; 1909, **42**, 1541.

[14] Dewar and Liebmann, English Patents 12981, 12982 (1913).

[15] Bedford, Dissertation, Halle, 1906.

[16] Hübl, J. Soc. Chem. Ind., 1884, **3**, 641, from Dingler's Polytech. J., 1884, pp. 253, 281.

[17] Wijs, Zeitsch. angew. Chem., 1898, **11**, 291. Ephraim, Analyst, 1895, **20**, 176, from Zeitsch. angew. Chem., 1895, **8**, 254; Hübl, loc. cit.

[18] Wijs, Ber., 1898, **31**, 750.

[19] Hanus, Zeitsch. Unters. Nahr. Genussm., 1901, **4**, 913.

[20] Lewkowitsch, Opus cit., vol. ii., 1914, p. 66.

[21] Sheppard, loc. cit. See also Lettenmayer, Chem. Zeit., 1893, **17**, 1506; Ballantyne, J. Soc. Chem. Ind., 1891, **10**, 29.

[22] Mastbaum, Zeitsch. angew. Chem., 1896, **9**, 719.

[23] This was first pointed out by Hazura, Zeitsch. angew. Chem., 1888, **1**, 312. Hazura and Grüssner, Monatsh., 1888, **9**, 180.

[24] Because the precipitate is more granular and proportionately more easy to deal with.

[25] Hehner and Mitchell, Analyst, 1898, **23**, 310.

[26] Ingle, J. Soc. Chem. Ind., 1911, **30**, 344.

[27] Sutcliffe, Analyst, 1914, **39**, 28, 388. See also Gemmell, ibid., p. 297.

[28] See Lewkowitsch, Opus cit., 1913, vol. i., p. 476. From Zeitsch. Unters. Nahr. Genussm., 1912, **23**, 684.

[29] Hehner and Mitchell, Analyst, 1895, **20**, 148.

[30] Wiley, J. Amer. Chem. Soc., 1896, **18**, 378; Gill and Hatch, ibid., 1899, **21**, 27; Jenkins, J. Soc. Chem. Ind., 1897, **16**, 194; Archbutt, ibid., p. 307.

[31] Fenaroli, Gazz. chim. ital., 1906, **36**, (2), 292.

[32] See Mackey, J. Soc. Chem. Ind., 1915, **34**, 595; Lloyd, ibid., p. 596.

[33] Lippert, Zeitsch. angew. Chem., 1898, **11**, 412; Weger, ibid., p. 502.

[34] Wise and Duncan, J. Ind. Eng. Chem., 1915, **7**, 202.

[35] Redman, Weith, and Brock, J. Ind. Eng. Chem., 1913, **5**, 630.

[36] Ingle, J. Soc. Chem. Ind., 1913, **32**, 639.

[37] This is neglecting the work of earlier investigators such as Cloez and Mulder, who employed thick layers of oil, and found but small percentage increases in weight for the reason already given in the text.

[38] See Friend, Introduction to the Chemistry of Paints (Longmans & Co.), 1910.

[39] Kronstein, Ber., 1916, **49**, 722.

[40] Sabin, J. Ind. Eng. Chem., 1911, **3**, 84.

[41] Täuber (Chem. Zeit., 1909, **33**, 85, 94) explains the cracking of paint surfaces by assuming the existence of an electrical tension caused in some indefinite manner by the fragments. Such an assumption is quite unnecessary for the linoxyn cannot be expected to shrink indefinitely without cracking.

[42] Friend, Proc. Paint Varnish Soc., 14th May 1914. The volatile products were absorbed by passage through weighed tubes of calcium chloride (for water) and caustic potash (for CO_2, etc.).

[43] Mulder, Die Chemie der austrocknenden Oele, Berlin, 1867, p. 109, etc. Compare also Olsen and Ratner, Eighth Int. Cong. Applied Chem., 1912, Section v. **12**, 165; Krumbhaar, Chem. Revue, 1913, **20**, 290.

[44] Sabin, loc. cit.; Gardner, J. Ind. Eng. Chem., 1914, **6**, 91.

[45] Mulder, Opus cit., p. 130.

[46] Fokin, J. Russ. Phys. Chem. Soc., 1907, **39**, 607; 1908, **40**, 276. Compare also Orloff, ibid., 1910, **42**, 658; 1911, **43**, 1509.

[47] Lippert, Zeitsch. angew. Chem., 1905, **18**, 94.

[48] Mulder, Opus cit., p. 115. The presence of acrolein has since been confirmed by Salway (Trans. Chem. Soc., 1916, **109**, 138).

[49] Sacc (Annalen, 1844, **51**, 213) thought that butyric acid was present in the vapours. This has since been confirmed by Gardner (Oil Colour Trades J., 1914, **45**, 1000).

[50] See Lidoff and Fokin, Chem. Rev., 1901, No. 6. Gardner (J. Ind. Eng. Chem., 1914, **6**, 91) thought he had proved the existence of carbon monoxide in the evolved vapours, but his method of experiment was faulty (see criticism by Klein, Chem. World, 1914, **3**, 250). The presence of carbon monoxide has been confirmed by King (J. Ind. Eng. Chem., 1915, **7**, 502).

[51] It is interesting in this connection to note that 0·6 per cent. of free and 9·8 per cent. of combined azelaïc acid was found in old, exposed rancid cotton-seed oil. The low free acid value confirms the view that rancidity is not due simply to hydrolysis of the glycerides but to oxidation to decomposition products. Nicolet and Liddle, J. Ind. Eng. Chem., 1916, **8**, 416. See also Gröger, Zeitsch. angew. Chem., 1889, **2**, 62; Scala, Chem. Zentr., 1908, i. 205; Bouley, ibid., 1907, ii., 1100; Ryan and Marshall, ibid., 1907, ii., 852; Cohn, Chem. Zeit., 1907, **31**, 855; Lauffs and Huismann, ibid., p. 1023.

[52] Mjöen, Forsch. Ber., 1897, **4**, 195; abstracted in Analyst, 1898, **23**, 42. Compare Spaeth, ibid., 1897, **22**, 46; Ritzert (Chem. Zeit., 1890, **14**, 1509), on the other hand, states that oxygen in the absence of light cannot induce rancidity.

[53] Lewkowitsch, Opus cit., 1913, vol. i., pp. 50-56.

[54] Tilchmann, Polytech. Centralblatt, 1858, p. 975.

[55] Mulder, Opus cit.

[56] Hird and Lloyd, J. Soc. Chem. Ind., 1912, **31**, 317.

[57] Sacc, Annalen, 1844, **51**, 213.

[58] Maumené, Compt. rend., 1882, **95**, 572; 1881, **92**, 721.

[59] Archbutt, J. Soc. Chem. Ind., 1886, **5**, 304.

[60] Tortelli, Chem. Zeit., 1909, **33**, 184.

[61] Archbutt, J. Soc. Chem. Ind., 1897, **16**, 310; Stiepel, Seifenfabrikant, 1911, **31**, 349, 393, 421, 445, 473, 501, 525.

[62] Marden, J. Ind. Eng. Chem., 1916, **8**, 121. See also Luginin and Koblukoff, J. Chim. phys., 1906, **4**, 489; 1907, **5**, 186. Luginin, Compt. rend., 1910, **150**, 915.

[63] Backer, Chem. Weekblad, 1916, **13**, 954.

[64] Mannich and Thiele, Ber. D. Pharm. Ges., 1916, **26**, 36 (taken from J. Soc. Chem. Ind., 1916, **35**, 548, which gives a useful abstract of the original paper).

SECTION V.

[1] Sacc, Ann. Chem. Pharm., 1844, **51**, 213. Sacc also concluded that linseed oil contains "margaric acid." The substance known by that name at that time has since been proved to be a mixture of palmitic and stearic acids of constant melting-point, and which cannot be separated by ordinary methods of crystallisation (Heintz, J. prakt. Chem., 1855, **66**, 1). True margaric acid, $C_{16}H_{33}.COOH$, does not appear to occur in nature (Holde, Ber., 1905, **38**, 1247). It has been prepared synthetically (Krafft, Ber., 1879, **12**, 1670. Le Sueur, Trans. Chem. Soc., 1904, **85**, 827).

[2] Schüler, Ann. Chem. Pharm., 1857, **101**, 252. The formulæ in the text have been transformed from the older style used by Schüler, who wrote $C_{32}H_{28}O_4$ and $C_{32}H_{32}O_4$ for linoleic and palmitic acids respectively.

[3] Mulder, Die Chemie der austrocknenden Oele, Berlin, 1867, pp. 40-48.

[4] See Gmelin, Handbuch der Chemie (Kraut), 1866, vol. vii., pp. 1230-1233. Palmitic acid had also been found previously, namely by Schüler. Myristic acid has not been confirmed by later investigators such as Haller and Morrell (refs. 5 and 6).

[5] Haller, Compt. rend., 1908, **146**, 259.

[6] Morrell, J. Soc. Chem. Ind., 1913, **32**, 1091.

[7] It is here assumed for purposes of calculation that the relative proportions of free acids in the oil are the same as those of their glycerides. The error is negligibly small, being much less than either the error of experiment or the variation between different samples of pure raw oil.

[8] Peters, Monatsh., 1886, **7**, 552.

[9] Dieff and Reformatzki, Ber., 1887, **20**, 1211.

[10] Hazura, Monatsh., 1876, **8**, 260.

[11] Hazura, ibid., 1888, **9**, 180; Zeitsch. angew. Chem., 1888, **1**, 312.

[12] Hehner and Mitchell, Analyst, 1898, **23**, 310.

[13] Morrell, J. Soc. Chem. Ind., 1915, **34**, 105.

[14] Schlicht, Seifenfabrikant, 1914, **34**, 673.

[15] U.S. Specifications, Bulletin No. 107; U.S. Department of Agriculture. See J. Ind. Eng. Chem., 1914, **6**, 164.

[16] It will be understood that these figures have been calculated by the present author from the foregoing data. They are not to be found, therefore, in the original memoirs.

[17] The reason for this is by no means clearly stated in the original memoir.

[18] Fahrion, Zeitsch. angew. Chem., 1903, **16**, 1193. Owing to the limitations of space it is impossible to discuss the data upon which Fahrion bases his conclusions as fully as the subject deserves.

[19] By the term linolenic acid is here understood both this acid and its isomerides, should the latter ultimately be proved to have a definite existence in linseed oil (see p. 57).

[20] Fahrion, Zeitsch. angew. Chem., 1910, **23**, 1106.

[21] Fokin, J. Russ. Phys. Chem. Soc., 1902, **34**, 501.

[22] Erdmann and Bedford, Zeitsch. physiol. Chem., 1910, **69**, 76.

[23] Bauer and Hazura, Monatsh., 1888, **9**, 459.

[24] Fahrion, Zeitsch. angew. Chem., 1910, **23**, 722.

[25] Ingle (J. Soc. Chem. Ind., 1913, **32**, 639) obtained analogous results with linseed oil itself.

[26] Engler and Wild, Ber., 1897, **30**, 1669; Engler and Weissberg, Ber., 1898, **31**, 3046; Engler, Ber., 1900, **33**, 1091.

[27] Quoted by Fahrion (ref. 28).

[28] Fahrion, Chem. Zeit., 1904, **28**, 1196.

[29] Engler and Frankenstein, Ber., 1901, **34**, 2933.

[30] See Grün, Ber., 1909, **42**, 3759.

[31] Orloff, Chem. Zentr., from J. Russ. Phys. Chem. Soc., 1910, **42**, 658.

[32] Salway, Trans. Chem. Soc., 1916, **109**, 138.

[33] It will be observed that the experimental evidence is based on the assumption that the increase in weight, or apparent oxygen figure (see p. 46), gives the total oxygen absorption. As has been shown, such is not the case. Further research is necessary to determine whether or not the error is sufficiently great to seriously affect the conclusions drawn.

[34] See Waele, Chem. World, 1914, **3**, 300; Ingle, ref. 25.

[35] Reid, J. Soc. Chem. Ind., 1894, **13**, 1020.

[36] Livache, Compt. rend., 1883, **96**, 260; 1886, **102**, 1167.

[37] Walker, U.S. Department of Agriculture, Bureau of Chemistry, Bull. No. 109; Chem. News, 1910, **102**, 57; Liverseedge and Elsdon, J. Soc. Chem. Ind., 1912, **31**, 207, etc.

[38] Fokin, Ref. Augsb. Seifens-Zeitung, **34**, 821, 822.

[39] For a useful account of these see Radcliffe and Palmer, J. Soc. Chem. Ind., 1915, **34**, 644.

[40] Lippert, Zeitsch. angew. Chem., 1898, **11**, 412, 431.

[41] Fahrion (Chem. Zeit., 1904, **28**, 1196) overlooks this fact in his discussion of the subject.

SECTION VI.

[1] Ingle, J. Soc. Chem. Ind., 1911, **30**, 344.

[2] Krumbhaar, Chem. Zeit., 1916, **40**, 937. Other useful data are given by Kitt, Chem. Rev., 1901, **8**, 40; Leeds, J. Soc. Chem. Ind., 1894, **13**, 203.

[3] Fahrion, Zeitsch. angew. Chem., 1892, **5**, 171.

[4] Fokin, Ref. Augsb. Seifens-Ztg., **34**, 821.

[5] Morrell, J. Soc. Chem. Ind., 1915, **36**, 105.

[6] Friend, Trans. Chem. Soc., 1917, **111**, 162.

[7] Compare Kronstein, Ber., 1916, **49**, 722; 1902, **35**, 4150. Also Fahrion's criticism, Ber., 1916, **49**, 1194.

[8] From German Standöle, since on standing the mucilage coagulates and separates (Lewkowitsch).

[9] Manufacturing details do not concern us here. Useful information is given by Hurst, Painters' Colours, Oils, and Varnishes (Griffin & Co.), 5th Ed., 1913.

[10] Mulder drew attention to this, and further showed that the apparent oxygen figure in sunlight is less than that in the shade. Die Chemie der austrocknenden Oele, Berlin, 1867, p. 130.

[11] Genthe, Zeitsch. angew. Chem., 1905, **18**, 615; 1906, **19**, 2087; German Patent, 195663, 6th January 1906.

[12] Uviol lamps are mercury vapour lamps made with special uviol glass which allows very short rays to pass through it.

[13] Hahn, Zeitsch. angew Chem., 1908, **21**, 1441.

[14] Procter and Holmes, J. Soc. Chem. Ind., 1905, **24**, 1287. See also Leeds, J. Soc. Chem. Ind., 1894, **13**, 203.

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