

University of Louisville

## ThinkIR: The University of Louisville's Institutional Repository

---

Electronic Theses and Dissertations

---

5-1922

### Linseed oil and its oxidation products.

Mary Louise Towles  
*University of Louisville*

Follow this and additional works at: <https://ir.library.louisville.edu/etd>

---

#### Recommended Citation

Towles, Mary Louise, "Linseed oil and its oxidation products." (1922). *Electronic Theses and Dissertations*. Paper 1451.  
<https://doi.org/10.18297/etd/1451>

This Master's Thesis is brought to you for free and open access by ThinkIR: The University of Louisville's Institutional Repository. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of ThinkIR: The University of Louisville's Institutional Repository. This title appears here courtesy of the author, who has retained all other copyrights. For more information, please contact [thinkir@louisville.edu](mailto:thinkir@louisville.edu).

University of Louisville

Linseed Oil  
and its  
Oxidation Products

A Dissertation

Submitted to the Faculty  
Of the Graduate School of Arts and Sciences  
In Partial Fulfillment of the  
Requirements for the Degree  
Of Master of Science

Department of Chemistry

By

Mary Louise Towles

1922

Linseed oil is the oil from the plant *linum usitatissimum*. It is not a new oil, for we read that the Greeks and Romans used it, not as it is used today, but as a food, and it is still used for that purpose in some countries, especially in Russia, Poland, and Hungary.

The oil was first introduced into the United States during the nineteenth century, and in 1810 there were two hundred eighty three linseed oil mills in only fourteen states. In those days the process of obtaining the oil from the seed was tedious, and the yield was poor, for the oil was extracted by means of the old-fashioned mill stones.

After the demand for linseed oil increased, oil had to be imported from foreign fields. Up until 1861 the output was one million gallons per year. Prior to that time the largest portion of the seed was grown and used only for the fiber, with the seed regarded as a by-product, but now the fiber itself is only a by-product, and the plant is grown for the seed. After 1865 the production of flax moved west from the middle states, where all of the yield of the United States had been grown. The demand increased greatly from year to year. In 1870 the industry received a great stimulus when the old mill stones used

for pressing were replaced by rolls, and in ten years the yearly crop was quadrupled. All the seed is now grown west of the Alleghanies, and the states in the east still send to India and Russia for seed.

Linseed is flat and oval in shape, with a slightly unpleasant odor. It contains 25 per cent albumin, 8 per cent water, 28-40 per cent oil. When the oil is expressed instead of extracted with a solvent the per cent of oil is 8-15 per cent less. The yield of oil also varies with the country from which the oil is imported. Russian oil gives 32-38 per cent oil, North American seed 36-38 per cent, Morocco 36-40 per cent, China 31-38 per cent. One bushel of seed gives about two and one half gallons of oil, by expression. The age of the seed also influences the yield of oil. As a rule, seeds from two to six months old give better yield than fresh seed.

Before the seed is pressed it is always stored, for it is found that the oil is less turbid and also less viscous if the seed has been stored for some time before expression. Great care must be taken in the storage of linseed. It deteriorates rapidly from moisture and often perishes entirely. To prevent this the seeds must be stirred and turned frequently.

They are kept in dry, cool, well ventilated rooms, and the piles of seeds are often turned completely over to keep them from mould or decay.

The seed, as it comes from the exporters, is always full of impurities—not only dust and chaff but also other seeds which may become mixed with the linseed, such as rape seed, mustard seed, also sand and earth. The chaff and dust can be removed by exhaust fans. Then the seed is put on an oscillating screen. The seeds drop through and leave the coarse impurities behind.

Before the oil can be extracted the cells or particles which hold the oil must be broken up. So heavy rolls are used to crush the seed. Often when the seed is unusually dry a small amount of water is added to make a homogeneous mass. The machinery in use today is a series of rolls, four in number, arranged one above the other. The seed is fed in between the two top rolls, and is then worked down between the second and third rolls. The weight of each roll rests on those below it, so that when the seed is between the third and fourth rolls it has the pressure of all three rolls upon it. In this way it becomes crushed

to a very fine meal.

The meal may be expressed cold, or it may be heated. A great deal of it is heated so as to make the oil run more smoothly. If moisture is also present the heat and moisture combined help break the cell walls, and loosen the gelatinous coating which covers the outside of the cells. The heat also tends to coagulate some of the albuminous material dissolved in the oil.

The oil was formerly heated over an open fire in an iron pan, or with hot water, but the danger of overheating was very great. The result was always a burnt oil or one with a strong odor, or a dark color. Today the meal is heated in a steam-jacket kettle, with the temperature carefully regulated.

Cold pressed oil makes a much better grade of oil than hot pressed oil. The color is lighter, but the yield is not quite so large, since the oil does not flow so easily, and for this reason the greater the per cent of oil is expressed hot. Cold pressed oil is used more for edible purposes than for the paint industry.

There are three general methods for obtaining the oil from the seed--rendering, extraction with a

solvent, and expression.

Rendering is the oldest method. It was used centuries ago by the natives of West Africa and other uncivilized countries in obtaining crude oil from the seeds. The meal was either heated over an open fire in a kettle, or was boiled with water and the oily layer run off. But this method seemed to change the constitution of the oil, and allowed many impurities to flow into the oil, and this process is never used today.

The extraction with a solvent is used extensively. The method as given by Ennis, is as follows:

The seed is not ground so fine as for expression with hydraulic press. It is then heated to 180° to drive off moisture. The meal is put into a percolator. The solvent (naphtha) is passed through a coil, with steam in the shell, to increase its solvent power. The naphtha then drops in on top of the coarse meal. It percolates through the meal and the solution of oil in the solvent is drained off at the bottom of the tank. This solution passes through the tubes surrounded by steam. This boils off the naphtha, which goes to the condenser to be used again, and the oil goes to a container. This process is carried

on for three days, for at the end of that time the greater part of the oil is extracted. The oil in the tank is then raised to high temperature to drive off any remaining naphtha.

The first extraction was carried out by Jesse Fisher, in 1843. He used carbon disulphide as a solvent, but the oil which he obtained had the odor of carbon disulphide, traces of sulphur were found precipitated in the oil, and the meal left behind was unfit for food.

Carbon tetrachloride has been used with some success as a solvent, as it has no unpleasant odor, is not poisonous, leaves no residue, has a low boiling point, and is not inflammable.

The first solvent was carbon disulphide, now in disuse, and the principal solvents used today are benzene, petroleum ether, ether, carbon tetrachloride, acetone, and recently liquid sulphur dioxide has been used with some success.

The solvent used must have certain characteristics. It must dissolve only the fatty portion of the oil, not the gum and mucilage. The solvent must be removed completely by distillation, so as to be entirely recovered, and must give no flavor to the oil.



There is some objection to extracting by means of a solvent. The meal left is no good for cattle food, It contains only 2-3 per cent of oil left after extraction process is complete, and the husks are not fit for food. Another trouble is the high cost of steam for the process. All these difficulties have not made the process the most popular one. In fact, today, very little oil is expressed by this method.

The best method for extracting the oil is by expression. The method was in use thousands of years ago, in a very crude way, but modern methods date from 1795, when Joseph Bramah invented the hydraulic press. The pressure is applied very slowly at first, and is gradually raised up to two tons per square inch. The cakes are collected, given a second heating, and pressed again.

The cake left from expression is very valuable as a cattle food. It is not used to any large extent in the United States, but is used extensively in the European countries, and all linseed cake made in the United States is shipped abroad. It is considered a valuable by-product of the linseed oil industry, often bringing from \$18 to \$25 per ton. The average composition is: s

Water-----	10-13 %
Protein-----	28-35 %
Oil-----	9-13 %
Carbohydrate-----	26-30 %
Fiber-----	7-10 %
Ash-----	6-9 %

The impurities found in linseed oil are of a varied nature, depending on the method of expression. Even if it is extracted by means of a solvent, different solvents dissolve out different materials, and different impurities come out at different temperatures.

Both organic and inorganic substances are dissolved in the oil. Of the inorganic impurities water and metallic salts are the most important. The water is easily removed when, during the refining process, the oil is heated to a high temperature. The mineral salts are usually precipitated and settle to the bottom of the tank during the refining process.

The organic impurities are not so easy to remove. These consist of protein, carbohydrates, gums, resins, enzymes, soaps, glycerin, lecithin, and the higher hydrocarbons. All of these except the proteins are present in very small quantities,

so that their presence does not seriously effect the oil. They are removed with the precipitation of the protein.

The protein material comes from the cells of the plant, and is dissolved in the oil. These proteins are soluble in water, and in dilute salt solution. They cause emulsions in the oil and form persistent emulsions when the oil is shaken with water. The oil is cleared of this protein material by adding salt solution or mineral acid. These precipitate the protein, and it settles to the bottom of the tank, carrying with it any other dissolved material. Filtration of the oil removes some of the impurities, that is, those held in suspension, but the proteins and the vegetable or animal gums are colloidal and cannot be filtered out.

Other oils are often present in linseed oil, due to the impurity of the seed before the oil is expressed. Oil of mustard seed is the commonest impurity. If this oil is present in large quantities the linseed loses its property of drying rapidly.

The refining of linseed oil can be done by numberless processes, in fact, the processes are too many and various to be enumerated here. The main

types of processes will be discussed briefly.

Mere filtration, after the oil has been allowed to settle, and the clear liquid drawn off, is often used for purification, and gives a very bright clear oil, which is quite satisfactory for ordinary paint work. The oil is often tanked to clarify it. It is put into large open tanks and kept at a temperature of 150 degrees, Centigrade. During the process air is blown through the oil by fans or blowing machines. This process gives a splendid clear oil, with no break on heating, but it is very slow and often chemical means of purification are resorted to.

Various types of chemicals are used in refining linseed oil. Alkaline solutions were once used in purifying, but today they have been replaced by other agents, because they saponify with the oil and form emulsions which are very persistent. Acids are used extensively, as well as zinc chloride. Certain solids, such as magnesia, Fuller's earth, powdered minerals are used, which by mechanical means carry down suspended materials and impurities in colloidal solution.

Wasl found a ~~satisfactory~~ method of refining

with sulphuric acid. Concentrated acid is added in a thin stream, one part acid to four hundred parts of oil. When this is thoroughly mixed, boiling water is added. The mixture is then allowed to stand and settle, the oil is drawn off, and three per cent dry sodium chloride is added. This takes out the water and settles to the bottom of the tank. The oil is then filtered through sacks of wheat bran.

Engleduc has a method of refining by means of ozone. The moisture is all removed from the oil and no heating is necessary to destroy the color of the oil.

The 'wet process' consists of passing steam through a mixture of linseed oil and hot water from one to two hours. This mixture is allowed to stand, and after several days it is found that the impurities form a white layer between the oil and the water layers. The oil is then drawn off from the water and is heated to 220 degrees to drive off any remaining water. Sometimes Fuller's earth or lead sulphate is added to bring down any colloidal matter or any coloring material.

In Nördlinger's process the organic fatty

acid salts of the heavy metals are dissolved in ten to twenty parts of vegetable or rosin oil. This solution, called refining oil, is added to the linseed oil. The oil seems to go into solution, but if it is allowed to stand a turbidity is soon noticed. The salts of the heavy metals are thrown out of solution and as they settle to the bottom of the tank the impurities are carried with them.

When linseed oil is allowed to stand a thick mucilaginous mixture settles to the bottom of the tank. This has been studied, but today the chemical character of the 'foots', as this sediment is called, technically, is not known. Eisenschymel has been doing some work on linseed foots and gives the following analysis.

Oil and insoluble portion	75.8 %
SiO <sub>2</sub>	none
CaO	3.26 %
MgO	4.99 %
K <sub>2</sub> O	10.27 %
P <sub>2</sub> O <sub>5</sub>	<u>1.08 %</u>
Total	99.60 %

The color of linseed oil is usually a pale yellowish shade. Of course, this varies with the

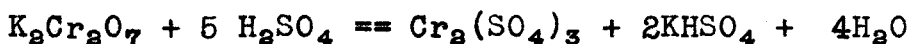
source of the oil, the extraction process used, and the refining process. But the requirements of the trade are becoming greater and greater with respect to the color of linseed oil. The reason offered is that they must have an oil which is absolutely colorless with white pigments, but when linseed oil is dried it is bleached absolutely colorless. On the other hand, linseed oil which has not been changed by bleaching agents is much more pure and harmless to pigments than bleached oil.

The principal bleaching agents employed today are sodium peroxide, hydrogen peroxide, chlorine, calcium chloride, potassium permanganate, potassium dichromate, ozone, sulphurous acid, and sodium thio-sulphate.

Bleaching with light is really the best method of bleaching, for in this way the oil is not changed materially. The only change is that the oil becomes somewhat thickened and slightly rancid, but the main objection to the method is the length of time which the process requires. The oil must be stored for several months before any bleaching takes place. Today the oil is placed in shallow tanks and exposed to the direct sunlight. If the rays of the sun can penetrate through

the whole depth of the oil the process can be completed in a much shorter length of time, usually in four to five weeks. The rays of the sun have the bleaching effect, and if the oil is kept in a dark place or in deep tanks the same process would take months. In case ozone is used instead of air, the process takes but four to five days. The oil is bleached by aspirating the ozone through the oil.

The basis of the action of the chemical agents is the action of the chlorine or the oxygen. In the case of the oxidizing agents, sulphuric acid or hydrochloric acid is added to free the oxygen or chlorine. With potassium dichromate the oil is bleached according to the following equations:



Only a small per cent of acid or oxidizing agent has to be added to get the desired effect, but even that small amount injured the oil.

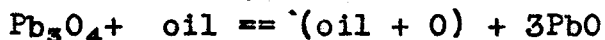
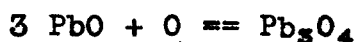
Oil is often bleached with Fuller's earth, which consists chiefly of silica, alumina, iron, and lime. This is added to the oil in a very small quantity and mixed with the oil for three to four hours, and kept at a temperature of 200 degrees. This process



is more or less mechanical, the Fuller's earth taking up any suspended material, and is not dependent on any chemical action.

Boiled oil formerly meant what its name implied--oil which had been boiled or heated to a high temperature, to rid it of impurities, and which had drier added to it. Today boiled oil is often not heated at all, but merely has drier added, though some of the manufacturers do heat the oil to a more or less high temperature before adding the drier. Litharge is the most common drier used today, although some concerns prefer the manganese and lead resinates. Litharge cannot be added in excess of one per cent. This much makes the oil dry and hard in five hours, if it is spread in thin layers.

Oil to which drier has been added dries in much less time than ordinary commercial refined linseed oil. This is not thought to be due to the addition of oxygen to the oil itself, but to the substances which are added which absorb oxygen from the air themselves and then transfer it to the oil, as shown by the following equations:



In making boiled oil the oil was once heated over an open flame to a high temperature, but this process makes the oil much darker. The oil begins to decompose, gets too thick, and the fumes cause great loss. The temperature to which the oil is heated has much to do with the drying power of the oil. Most of the oil is heated to 270 degrees, for the varnish trade requires an oil which does not break at 270-280 degrees--that is, shows no coagulation or solid material dropping out at that temperature. The drier is added while the oil is hot and then the mixture is allowed to settle for four or five days. Another process is to heat the oil to 125-130 degrees by means of super-heated steam but this latter process has not come into common use.

Boiled oil has altered properties from raw oil. In the settling process the oil becomes lighter in color and somewhat thickened. This latter property is especially true of manganese dried oil, while lead dried oil always deposits flocs. In consistency boiled oil should be only slightly more viscous than raw oil. The temperature must be watched carefully,

as this greatly influences the viscosity of the oil. In color boiled oil varies from pale yellow to a reddish brown, depending on the method of boiling and the drier used. A dark color is usually a good indication of a too high temperature. Manganese driers give pale oil while litharge and red lead give a dark oil. Boiling by means of superheated steam also gives a pale oil. The trade requires a clear transparent oil and this is procured only by letting the oil stand.

The requirements as to length of time for drying vary with different localities or different purposes to which the oil is to be put. It can be made to dry in so short a time as five to six hours, but the usual length of time is eighteen to twenty-four hours.

Blown oil is made by blowing superheated steam through the oil at a temperature of 450 degrees. The breakable part of the oil is then decomposed and passes off as vapor. There is also a sediment of insoluble impurity which as a rule consists of mucilage and protein which settles to the bottom of the tank on cooling. This oil is then centrifuged to separate out solid material and then treated with

Fuller's earth to lighten the color. The oil is then filtered and cooled to 16 degrees below zero. The solid stearin separates out at this temperature and after filtration the oil is ready for the market. This oil is very highly refined and very pure. It is used principally in varnish making.

Stand oil is a very heavy viscous form of linseed oil, used principally in making enamel and linoleum. The oil probably originated in Holland, where linoleum was first made. The oil is heated to 550 degrees Fahrenheit, care being taken that the oil is sufficiently refined not to show any break at that temperature. The oil is kept at 550 degrees until it becomes heavy and viscous. The specific gravity changes from 0.93 to 0.98. At this point a small quantity placed on a piece of glass and allowed to cool 'piles' or stands up in a mound and runs very slowly. A small amount of drier, usually litharge, is added while the oil is at 550 degrees and the oil is then allowed to cool gradually. More than 0.1 per cent of drier is never used, since the object of the process is to keep the light color of the oil, and more drier would tend to darken the oil. Cobalt is the best drier in use today. In this process

it is thought that the oil polymerizes, for it always thickens, and upon analysis it is found that the molecular weight becomes either double or triple what it was in the original oil. Fahrion found that if he heated linseed oil to a high temperature a substance of molecular weight approximating 2000 was found.

Linseed oil is liable to adulteration in various ways, depending on the price of the oil as well as of the adulterants. The most probable adulterants are drying oils, such as candle nut oil, safflower oil, sunflower oil, and soya bean oil, hydrocarbons, cottonseed oil, nigerseed oil, tung oil, fish oil, hempseed oil, rape oil, mineral oils, rosin and rosin oils.

Fish oils can often be detected by odor, especially by rubbing the oil between the hand. Another test for fish oil is the phytosterol acetate test, or Morrell's test,<sup>10</sup>

Rosin oil can be detected by the sulphuric acid color test. Pure oil gives a dark brown clot, while adulterated oil gives a red clot. The unsaponifiable number gives a reliable test,<sup>11</sup> Rapeseed oil can be detected by the jelly-like mass formed on heating the oil to 300 degrees. Cottonseed oil is detected by the Halphen color reaction,<sup>12</sup> The Elaidin

test is often used for the purity of an oil. A great per cent of non-drying oil gives a solid mass with  $\text{HNO}_2$  (nitrous acid) while a great per cent of drying oil gives a liquid product with nitrous acid.<sup>13</sup>

Of course, all the adulterants seriously effect the drying of the oil. Mixed with rosins the oil dries but it dries soft and soon perishes, on account of this softness. With mineral oil present the oil dries but the mineral oil separates out and rises to the surface of the film. Fish oil does not dry at all.

Adulterations have a noticeable effect on all of the characteristics of linseed oil. The specific gravity is often not changed, for by adding some of an oil of higher specific gravity and some of lower specific gravity the final result would not be changed even with great adulteration.

The film test is often used for detection of adulteration, the extent of drying varying in proportion to the amount of adulteration. The insoluble bromide value is an important test for purity, for the most of the adulterants used give no insoluble bromides. <sup>14</sup>

The American Society for Testing Materials

gives the following specifications for linseed oil,<sup>s</sup>

<u>Raw Oil</u>	Maximum	Minimum
Specific Gravity, $\frac{15.5}{15.5}$	0.936	0.932
Specific Gravity, $\frac{25}{25}$	0.931	0.927
Acid number	6.00	-----
Saponification number	195.00	189.00
Unsaponifiable matter, percent	1.50	-----
Refractive Index	1.4805	1.4790
Iodine number, Hanus	-----	180.00
<u>Boiled Oil</u>		
Specific Gravity, $\frac{15.5}{15.5}$	0.945	0.937
Acid number	8.00	-----
Saponification number	195.00	189.00
Unsaponifiable matter, percent	1.5	-----
Refractive Index	1.484	1.479
Iodine number, Hanus	-----	178.00
Ash, percent	0.7	0.2
Manganese, per cent	-----	0.03
Calcium, per cent	-----	0.8
Lead, per cent	-----	0.1

The methods of tests, as recommended by the American Society for Testing Materials are as follows:

General—"Should be made on oil which has been fil-

tered through paper in laboratory at 60-80 degrees Fahrenheit immediately before weighing out."

Specific Gravity-use pyknometer, capacity 25 cubic centimeters. Make test at 15.5 or 25.5 degrees Centigrade.

Acid Number<sup>16</sup>-method given in Holley. Express in milligrams of potassium hydroxide per gram of oil,<sub>6</sub>

Saponification Number-Expressed as with acid number,<sub>7</sub>

Unsaponifiable Matter-Boemer's method<sub>18</sub>

Refractive Index-use Abbe Refractometer, at 25 degrees Centigrade .

Iodine Number-use Hanus method<sub>19</sub>

The elementary composition of linseed oil varies with the method of extraction from the seed.

	Carbon	Hydrogen	Oxygen
Cold drawn	78.11	10.96	10.93
Hot drawn	75.27	10.98	13.85

The oil is thought to contain from ten to thirteen per cent solid fatty acids, that is, stearic, palmitic, and myristic, and eighty-eight to ninety per cent liquid fatty acid glycerides.<sub>20</sub> Hazura and Grüssner<sub>21</sub> give the following composition

Oleic acid	5 %	linolenic acid	15 %
linoleic acid	15 %	iso-linolenic"	65 %



Fahrion gives the following composition:

solid fatty acids	8.5 %	linolic acid	30.0 %
oleic acid	17.5 %	linolenic acid	38.0 %

Linseed oil solidifies at 27 degrees below zero, but this varies with the amount of free fatty acids present. At 25 degrees below zero stearin crystallizes out. Linseed oil flashes at 450-500 degrees. It is soluble in acetone, petroleum ether, ethyl ether, carbon disulphide, chloroform, carbon tetrachloride, turpentine, benzene, and petroleum, and moderately soluble in alcohol. The oil is given its yellowish color by the green chlorophyll and red erythrophyll and xanthrophyll dissolved in the oil from the seed. The bleaching of linseed oil is dependent upon the changing of this coloring matter into the pale yellow type of chlorophyll.

Linseed oil contains various solid fatty acids, such as palmitic, myristic, butyric, valerianic, and caproic acid glycerides.

Myristic acid,  $C_{13}H_{27}COOH$ , was found by Mulder, but later investigators<sup>22, 23</sup> doubt its existence in linseed oil.

Palmitic acid,  $C_{15}H_{31}COOH$ , was found by Schuler<sup>24</sup> and later confirmed by Mulder and others<sup>25, 26</sup>

Stearic acid,  $C_{17}H_{35}COOH$ , was first shown to be present by Umverdorben<sub>24</sub>. Mulder did not find it, but later workers did<sub>25</sub>.

Arachidic acid,  $C_{19}H_{39}COOH$ , was found to be present as arachin in linseed oil. Haller found arachidic acid<sub>25</sub> and it was early worked on by other chemists<sub>27</sub>.

The unsaturated fatty acids present are of three types—those with one double bond, those with two, and those with three double bonds.

The principal acid with one double bond of the type formula  $C_nH_{2n-1}COOH$  is oleic acid. This acid on oxidation in alkaline solution with potassium permanganate gives di-hydroxy-stearic acid, formula  $CH_3(CH_2)_7CH=CH(CH_2)_7COOH == CH_3(CH_2)_7\underset{OH}{CH}-\underset{OH}{CH}(CH_2)_7COOH$

The acid may be removed from linseed oil by precipitating it as its lead salt. The lead salts of the unsaturated acids are soluble in ether, while the salts of the saturated acids are insoluble. This acid has one ethylene linkage, that is, one double bond of the type  $\underset{H}{R}C=\underset{H}{CR}$ , R representing saturated radicles.

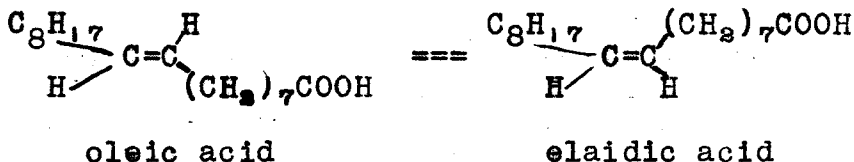
Oleic acid is a colorless acid, with no effect on litmus. On exposure to air and sunlight

it turns yellow. After sometime it becomes rancid and forms decomposition products, consisting mainly of formic, azelaic, and di-hydroxy stearic acids,<sup>28,29</sup> When oleic acid is heated with hydriodic acid and phosphorus stearic acid results<sup>30</sup>

The presence of only one double bond in oleic acid is proved by its power to absorb only two atoms of bromine or iodine, giving di-brom or di-iodo stearic acid<sup>31</sup>. Also, its oxidation with alkaline permanganate giving di-hydroxy stearic acid proves this formula. Hazura was the first to make the rule that unsaturated acids absorb as many hydroxyl groups as they possess free valency, giving hydroxy acids of same number of carbon atoms as the original acid<sup>32</sup>. Therefore, knowing stearic acid to be  $C_{17}H_{33}COOH$ ,  $C_{17}H_{33}Br_2COOH$ , or  $C_{17}H_{33}(OH)_2COOH$ , oleic acid must be  $C_{17}H_{33}COOH$ . There was formerly some discussion as to the place of the double linkage in the molecule. The old formula was  $CH_3(CH_2)_{14}CHCHCOOH_{33}$  but Baruch established the following formula,  $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ , which is now the accepted formula.

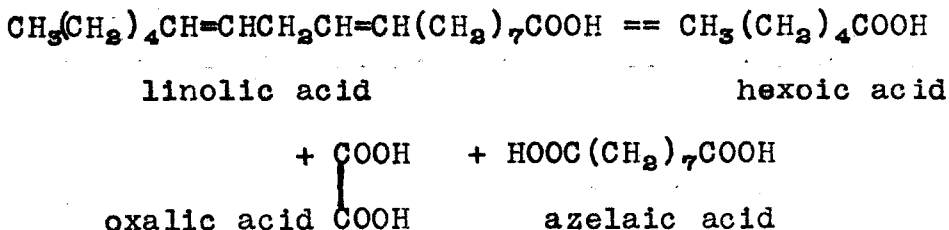
Oleic acid is present in linseed oil as its tri-glyceride. Nitrous acid changes it to its isomeride elaidin, the triglyceride of elaidic acid,

which is isomeric with oleic acid.



Linolic acid is a member of the unsaturated series  $\text{C}_n\text{H}_{2n-3}\text{COOH}$ , with two double bonds. It composes about fifteen per cent of linseed oil. This acid was thought by Mulder to be the same as linolenic, and he called the mixture linoleic acid. Hazura first found that linolein was a mixture of linolin and linolenin, the glycerides of linolic and linolenic acids, respectively.

Linolic acid gives a tetrabrom derivative  $\text{C}_{17}\text{H}_{31}\text{Br}_4\text{COOH}$   $\text{34}$  absorbs oxygen from the air, and forms a solid resinous body. With hydriodic acid and phosphorus it gives stearic acid  $\text{35}$ . On oxidation with alkaline permanganate it goes to tetra hydroxystearic acid, or sativic acid,  $\text{C}_{17}\text{H}_{31}(\text{OH})_4\text{COOH}$   $\text{36}$ . Goldsobel was the first to establish the formula for linolic acid. He worked on the oxidation of sativic acid and got azelaic, oxalic, and hexoic or caproic acids. This he could explain if he assumed the following formula for the acid:



This formula has recently been confirmed by optical methods<sub>37</sub>

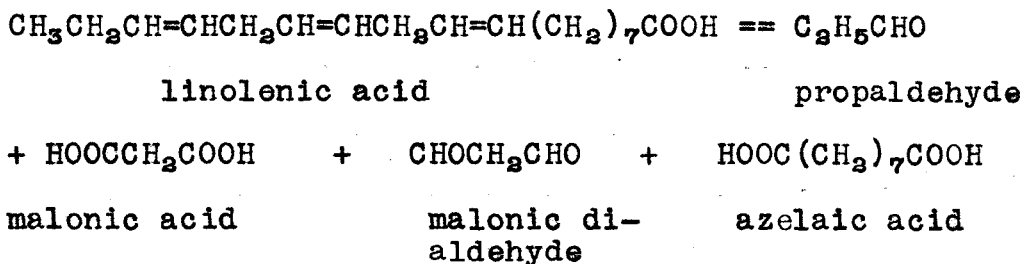
Some evidence has been given as to the possible presence of two stereo-isomerides of linolic acid in linseed oil, but the question is still being debated<sub>38</sub>

Linolenic acid,  $C_{17}H_{29}COOH$ , belongs to the series  $C_nH_{2n-5}COOH$ , with three double bonds or ethylene groups in the molecule. This acid in the form of triglyceride forms fifteen per cent of linseed oil, while its isomer, iso-linolenic acid forms sixty-five per cent of the oil. It was first found by Hazura<sub>38</sub> It gives a crystalline hexa-bromide derivative. The two isomeric acids are called alpha- and beta-linolenic acids. Erdmann and Bedford<sub>39</sub> did the first work on these isomerides. Linolenic acid absorbs oxygen from the air very rapidly, acrolein being given off<sub>40</sub> Oxygen is absorbed much faster by linolenic acid than by linolic, and on the percentage composition, with respect to linolenic acid, depends the rate of oxidation of linseed oil. Therefore, the higher the per cent of linolenic acid the higher the rate of oxidation.

With alkaline permanganate linolenic acid gives two hexa-hydroxy acids, known as linusic and

iso-linusic acids<sub>34</sub>

Goldsobel first established the position of the double bonds<sub>37, 41</sub>. He oxidized it with alkaline permanganate.



Erdmann and Raspe later confirmed Goldsobel's formula<sub>42</sub> but Rollett has since shown that these are only isomeric oxidation products and Rollett claims that this does not in any way show the presence of two different acids in linseed oil.

Like all fatty acid glycerides, linseed oil reacts with alkali to form a soap and free glycerine.

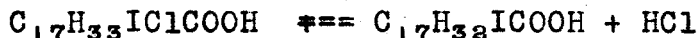
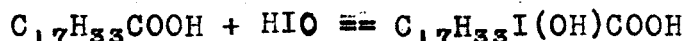
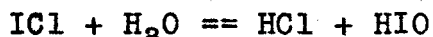


This reaction is taken advantage of in the determination of the saponification number, and of the unsaponifiable matter. Lewkovitsch even succeeded in hydrolyzing the oil to a remarkable degree in eight hours when he subjected it to steam, with no alkali present.

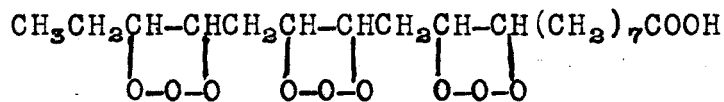
Hydrogen has no effect on the oil under ordinary

conditions, but when a catalyst, such as nickel, platinum, or palladium are used the hydrogen gas is absorbed quite readily by the oil, the unsaturated radicals being saturated by the entering hydrogen.

Iodine is slowly absorbed by linseed oil if a solution of iodine and mercuric chloride in alcohol is added to the oil dissolved in chloroform or carbon tetrachloride. The reaction is thought to occur in the following manner, one atom of chlorine and one of iodine attaching to each double bond<sup>44</sup>



Linseed oil readily absorbs ozone at low temperatures, one molecule of ozone being added to each double bond. These ozonides are believed to have the following structure:



When linseed oil is exposed to the air it gradually absorbs oxygen, yielding an elastic rubberish solid mass, called linoxyn. Mulder, a Dutch chemist, in 1867, was the first man to get any definite

results on the oxidation of linseed oil. From his investigations of different drying oils he drew the following conclusions:

The important constituent of linseed oil is linolein,  $C_3H_5O_3(C_{32}H_{27}O_2)_3$ , composed of linoleic acid,  $HOC_{32}H_{27}O_2$ , set free by saponification.

The principal substances produced by the drying of linseed oil were thought by Mulder to be linoleic anhydride, a slimy substance, like India rubber, linoxic acid,  $C_{32}H_{25}O_9OH$ , formed by the oxidation of linoleic acid, linoxyn,  $C_{32}H_{27}O_{11}$ , transformed by alkali into linoxid acid.

Hazura and Bauer worked on hempseed oil, obtaining hempolic acid. This acid is of the series  $C_nH_{2n-4}O_8$ , and according to this analysis it has the same composition as linolic acid,  $C_{18}H_{32}O_8$ . Sunflower oil, also, consists of glycerides of linolic and oleic acids, with the latter in very small proportions, so that the oil is very suitable for study of linolic acid. Hazura and Bauer took up the work where Mulder left it and discovered that linoleic acid is a mixture of four different fatty acids, eighty per cent linolenic acid, together with isolinolenic, linolic, and oleic acids. Hazura stated that "the acids of drying oils



all behave toward the oxygen of the air in a similar manner, the time of drying depending on the proportion of linolic acid to linolenic acid". Linolenic acid is the more unsaturated acid; therefore the higher percentage of linolenic the more rapid the rate of drying.

Mulder divided the drying of linseed oil into two periods: first, when the solid linoxyn was formed, when the oil dries but is elastic, and second, linoxyn is changed to a compound with more oxygen, but the layer becomes brittle and breaks.

He found that the oil when spread in thin layers attained a maximum in several days. The oil was found to increase in weight on drying, due to the absorption of oxygen. This absorption is due to two things: the absorption of oxygen by substances such as manganese borate in the oil, and the actual absorption of oxygen from the oxides, added as driers.

Weger and Lippert continued Mulder's work on the drying power. They of course, did not get absolute results, for temperature, light, thickness of the film, air, etc. effect the drying of the oil, but the results which they obtained were the average of a whole series of experiments carried out under conditions

as similar as they could obtain. Weger weighed the films, spread on pieces of glass, at different times during the period of oxidation. He found that the greatest weight occurred just at the time when the layer did not adhere to the finger when it is pressed lightly. He found that oxidation did not stop at this point, but merely that the oil did not increase in weight beyond that point, that is, after two to twenty-four hours. This he attributed to the fact that the amount of volatile products given off, carbon dioxide and water, corresponded to the oxygen absorbed. Weger got a maximum increase in weight, varying between 16.8 per cent to 19.9 per cent of the total weight of the oil. This was not found to be the case with boiled oil. The rate of absorbing the oxygen was higher, with boiled oil, that is, it dried better and faster, but the total amount absorbed was the same.

Halphen studied the work of Mulder and of Hazura and Bauer and drew the following conclusions:

1. The acids of the drying oils behave in the same manner as the glycerides.
2. The oxygen absorbed saturates the unsaturated bonds and also causes the formation of alcoholic products.

3. The products of oxidation are solid substances, insoluble in ether, which with alkali give compounds soluble in ether. Halphen was unable to tell whether the anhydrides are formed by condensation of two molecules with the elimination of water or by the elimination of water between the carboxyl group and a peroxide group of the same molecule.

4. Linolic and linolenic acids are the ones which take part in the oxidation. Oleic acid forms no solid products, and has no part in the reaction.

5. The oxidation begins on the glycerin, the part combined with oleic, palmitic and myristic acids.

Livache also worked on the oxidation, and got very accurate results. He tested the oil with substances that would increase their drying properties. He exposed the films for two years, analyzing the sample for increase in weight and per cent of insoluble acids. He found that the drying oils are changed to solid substances and that the non-drying oils approach certain of the drying oils. The principal factors influencing the drying of an oil are, according to Livache,

1. Degree of purity of the oil.
2. Time elapsed since extraction of the oil from the seed.
3. Manner in which the oil has been stored.
4. Temperature at which the oxidation takes place.
5. Addition of drier, and type and amount of drier used.

The influence of light on the drying of linseed oil was first studied by Cloes, who passed light through colorless, blue, red, green and yellow glasses. He found oxidation most rapid under colorless glass and least rapid under yellow glass.

Moisture seems to have little effect on the drying of linseed oil, according to most authorities, but De Waele<sup>47</sup> says that it causes the hydrolysis of peroxides during the latter part of oxidation.

If linseed oil is poured on cottonwool and allowed to oxidize a great deal of heat is set free, enough to cause a spontaneous combustion. This is due to the heat of oxidation, and depends on the rate of oxidation of the oil, boiled oil rising to a higher temperature than raw oil.

A great deal of work has been done on the percentage composition of linseed oil. Mulder was the first to work on this and his results<sup>47</sup> were as follows:

Unsaponifiable matter	1.00 %
Saturated acids	9.40 %
Oleic acid	9.40 %
Linoleic acid	75.80 %
Glycerol radicle	4.30 %
<hr/>	
Total	100.00 %

Hazura next worked on the proportions and found the unsaturated acids to be<sub>48</sub>

Oleic acid	5.00 %
Linolic acid	15.00 %
Linolenic acid	15.00 %
Iso-linolenic acid	65.00 %
<hr/>	
Total	100.00 %

According to Hazura's figures, the percentage composition of the oil would then be,

Unsaponifiable matter	1.00 %
Saturated organic acids	8.60 %
Oleic acid	4.30 %
Linolic acid	12.90 %
Linolenic acid	68.90 %
Glycerol radicle	4.30 %
<hr/>	
Total	100.00 %

Fahrion, in 1910, after carefully study-

ing all the data then available, concluded that the average composition was,

Unsaponifiable matter	0.60 %
Saturated organic acids	9.30 %
Oleic acid	17.50 %
Linolic acid	30.00 %
Linolenic acid	38.00 %
Glycerol radicle	<u>4.00 %</u>
Total	100.00 %

When linseed oil dries a tough elastic substance called linoxyn is formed. Its composition has not yet been determined, because of the fact that it does not enter into solution without decomposition. Its caoutchouc-like character is due to the large molecule formed, linseed oil 870, and linoxyn 1000, in comparison with the fatty acids, 280. It is absolutely insoluble in water, immediately saponifies with potassium hydroxide. Clöes found in linoxyn fatty acids and an insoluble body. Livache subjected it to various solvents. He found that at first no action was observed, but on continued action the substance swelled up and the liquid became noticeably colored. When the dried film is ground up a different action was noticed. The mass swelled up and divided into small particles, forming a sort of

salve. If more solvent is added the particles divide up and the liquid becomes colored. If the mass is separated from the colored liquid and the latter is evaporated it is found that a sticky rubbery substance remains behind, which adheres to the fingers. When the insoluble mass is dried an elastic mass which can be rubbed into particles between the fingers is formed.

The author worked on the solubility of lin-oxyne in various solvents. The differences or variations in solubility seem to be due to the amount of unoxidized oil remaining in the film.

<u>Ether Solubility</u>	I	II	III
Per cent insoluble	65.14	65.19	64.93
Per cent soluble	34.78	34.80	35.00
<u>Alcohol Solubility</u>			
Per cent insoluble	43.65	44.95	43.90
Per cent soluble	56.91	54.82	56.02
<u>Carbon Disulphide Solubility</u>			
Per cent insoluble	75.06	74.85	74.82
Per cent soluble	24.82	25.15	24.455
<u>Carbon Tetrachloride Solubility</u>			
Per cent insoluble	65.27	65.12	64.91
Per cent soluble	34.77	34.82	34.88

Various oxidizing agents were added to lin-

seed oil, and the effect noted carefully.

10 cubic centimeters of concentrated nitric acid were added to 100 cubic centimeters of the oil and the mixture put on a water bath for twenty-four hours. The mixture turned dark immediately and after the mass had been allowed to cool it was found that a solid substance had been formed. This substance was removed from the oily mixture and examined. It was found that it was linoxyn, the same substance formed by air oxidation of linseed oil.

Sulphuric acid and potassium dichromate were added to another 100 cubic centimeters of oil. The mixture immediately turned very dark. No solid substance was formed from this oxidation, however.

The effect of hydrogen peroxide was also investigated. 20 cubic centimeters of hydrogen peroxide were added to 50 cubic centimeters of linseed oil. The oil became lighter in color, but showed no oxidation products, showing that hydrogen peroxide is too weak an oxidizing agent, and merely had a bleaching effect on the oil.

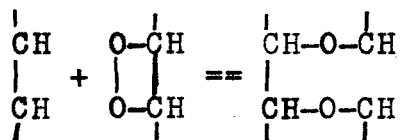
Sulphuric acid and potassium permanganate also caused the oil to turn dark in color. The effect was analogous to that of sulphuric acid and



potassium dichromate. No solid oxidation product was formed.

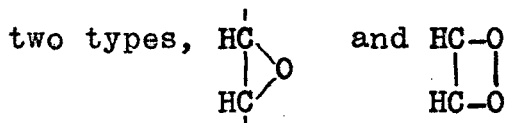
Hazura and Bauer<sup>51</sup>, stated that the glycerol content of the residue was five per cent of the original weight of linoxyn, while Fahrion found the same results<sup>52</sup>

Weger suggested that peroxides are formed during the oxidation of linseed oil. Oleic acid, with one double bond, absorbs no oxygen, linolic, with two double bonds, absorbs one molecule of oxygen, and linolenic and isolinolenic, with three, absorbs two molecules of oxygen. Thus the oxidation products are peroxylinolic acid,  $C_{17}H_{31}O_2COOH$ , and diperoxylinolenic acid,  $C_{17}H_{29}(O_2)_3COOH$ . These acids may undergo several changes, as  $\begin{array}{c} CH-O \\ | \\ CH-O \end{array} == \begin{array}{c} CH-OH \\ | \\ C=O \end{array}$ , giving a hydroxyketoxyacid radical, or anoxidized and an unoxidized radical may combine.



Fahrion believes that linoxyn consists of peroxylinolic, di-peroxy-linolenic acids, partially changed to ketoxy acids<sup>53</sup>

Orloff believes that oxidized bonds are of



Salway believes that the central double bond is unaffected on account of its greater stability, and that a dioxygenide is formed. This, he thinks, yields aldehydes which polymerize to form linoxyn, a small quantity of carbon monoxide and carbon dioxide, and acrolein being evolved at the same time.<sup>40</sup>

Fahrion<sup>58</sup> gave as his theory as to the oxidation of fatty acids the following: unsaturated acids with one double bond on oxidation give only volatile products, fatty acids with several leave one intact, add oxygen to the others, and absorb some extra oxygen to form hydroxyl groups, giving hydroxy-acids, insoluble in petroleum ether, soluble in alcohol and in benzene. Fahrion's work has not, however, been proven, as yet and the evidence is not sufficient to establish his theory as fact. The question is still under discussion. Other theories have been advanced, but none give conclusive enough evidence to draw a conclusion at the present time.

## Bibliography

- 1 Ennis, Linseed Oil and Other Seed Oils, pg.177-8
- 2 Ibid
- 3 Toch, Chemistry and Technology of Paints.
- 4 Andes, Drying Oils, Boiled Oils, etc. pg.125
- 5 Ibid, pg. 131
- 6 Ibid, pg. 137
- 7 Eisenschyml, Journal Ind. and Chem. Eng. Jan. 1910
- 8 Niegemann, Chem. Zeitung, 29, 465, 1905
- 9 Bömer and Winter, Lewokvitsch, Chem. Tech. and  
Analysis of Oils, Fats and Waxes
- 10 C. A. Klein, Allen's Commercial Organic Analysis,  
Vol. II, pg. 340
- 11 Lewkovitsch, Chemical Technology and Analysis of  
Oils, Fats and Waxes, Vol. III, pg. 203
- 12 Ibid, Vol. III, pg. 204
- 13 Ibid, Vol. I, pg. 461
- 14 Allen's Commercial Organic Analysis, Vol. II, pg 342
- 15 Holley, Paint Vehicles, Japans and Varnishes
- 16 Bulletin 107, 1908, Dept. of Agriculture, Bureaus  
of Chemistry, pg 142
- 17 Ibid, pgs. 137, 138
- 18 Boemer, Nibbelobde, Handbuch der Öle und Fette,  
pgs. 261, 262

- 19 Bulletin 107, 1908, Dept. of Agriculture, Bureau of Chemistry, pg. 136
- 20 Williams, Analyst, 1898, 23, pg 253
- 21 Hazura and Bauer, Allen's Commercial Organic Analysis, Vol.II, pg. 330
- 22 Haller, Compt. Rend, 1908, 146, pg. 259
- 23 Morrell, J. Soc. Chem. Ind. 1913, 32, pg. 1091
- 24 Gmelin, Handbuch der Chemie(Kraut), 1866, 7, pgs. 1230-33
- 25 Haller, Compt. Rend., 1908, 146, pg. 259
- 26 Morrell, J. Soc. Chem. Ind., 1913, 32, pg. 1091
- 27 Baczewski, Monatsch, 1896, 17, pg. 530
- 28 Scala, Stz. Sperim. Agri. Ital.1897, 30, pg. 613
- 29 Canzoniri and Bianchini, Annali Chim. Appl. 1914, 1, pg. 24
- 30 Wilde and Reychler, Bull. Soc. Chim. 1889, (3), 1, pg. 295
- 31 Overbeck, Annalen, 1866, 140, pg. 39
- 32 Haxura, Monatsch., 1887, 8, pg. 260
- 33 Overbeck, Annalen, 1866, 140, pg. 38
- 34 Hazura and Brüssner, Monatsch., 1888, 9, pg. 180
- 35 Peters, Monatsch., 1886, 7, pg. 552
- 36 Rollett, Zeitsch. Physiol. Chem., 1909, 62, pg. 410
- 37 Goldsobel, J. Russ. Phys. Chem.Soc., 1906, 38, pg .904

- 38 Monatsch, 1887, 8, pg. 260
- 39 Erdmann and Balford, Zeitsch. Physiol. Chem. 1911,  
74, pg. 179
- 40 Salway, Trans. Chem. Soc., 1916, 109, pg. 138
- 41 J. Russ. Phys. Chem. Soc., 1910, 42, pg. 55
- 42 Ber., 1909, 42, 1334
- 43 Zeitsch. Physiol. Chem., 1909, 62, pg. 424
- 44 Wijs-Zeitsch. Angen. Chem., 1898, 11, pg. 291,  
1895, 18, pg. 254
- 45 Andes, Drying Oils, Boiled Oils, Etc. pg. 7
- 46 J. Soc. Chem. Eng., 34, 1920, pgs. 48-50
- 47 Die Chemie der Austrocknenden Oele, Balin, 1867,  
pgs. 40,48
- 48 Monatsch. 1876, 8, pg. 260
- 49 Zeitsch. Angen. Chem., 1910, 23, pg. 722
- 50 Feliz Fritz, Kunststoffe, 1919, 9, pgs. 272-3
- 51 Monatsch. 1888, 9, pg. 459
- 52 Chem. Umsch. 1920, 27.
- 53 J. Russ. Physiol. Chem. Soc., 1910, 42, pg. 658
- 54 Waele, Chem. World, 1914, 3, pg. 300
- 55 Ingle, J. Soc. Chem. Ind., 1913, 32, pg. 639
- 56 Chem. Umschau, 1920, 27, pgs. 158-160, 1921, 28, pgs.  
5-7, 20-21