The Production and Properties of Oxidized Fatty Oils.

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THE PRODUCTION AND PROPERTIES
OF
OXIDIZED FATTY OILS

by

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A DISSERTATION
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INTRODUCTION

When we speak of fatty oils, we embrace a large group of natural products consisting essentially of esters of the higher fatty acids in combination with glycerol. Roughly, we may class certain ones as liquid fats or fatty oils, and others as solid fats. A more precise subdivision would lead to the following classification:

- I. Liquid fats and fatty oils
  - A. Vegetable oils
    - 1. Drying oils
    - 2. Semi-drying oils
    - 3. Non-drying oils
  - B. Animal oils
    - 1. Marine animal oils
      - a. Fish oils
      - b. Liver oils
      - c. Blubber oils
    - 2. Terrestrial animal oils
- II. Solid fats
  - A. Vegetable fats
  - B. Animal fats
    - 1. Drying fats
    - 2. Non-drying fats

In the field of protective coatings we are concerned only with those liquid fatty oils which possess some so-called "drying" ability. Of these liquid fats, linseed oil is by far the most widely used, the most widely exploited, and the most widely studied.

HISTORICAL

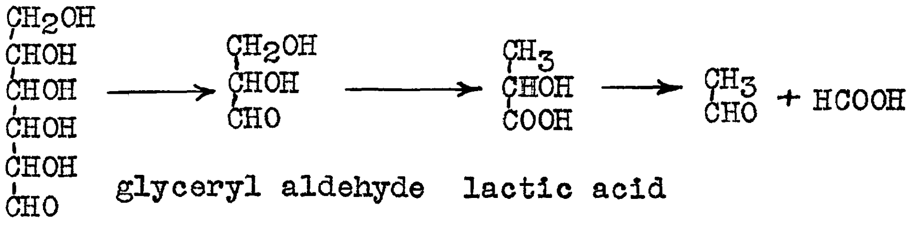
I. The Production Of Raw Oil From The Seed

While there is little doubt of the use of linseed oil from early times, no unmistakable mention was made of this oil earlier than the fifth century, when it was incidentally mentioned by Aetius, a Greek medical writer. On the contrary, other oils, in particular walnut oil and poppyseed oil, were described by Dioscorides five hundred years earlier.

Even today, the formation of these oils in nature is not understood. Variations in climate are known to produce changes in the unsaturated nature of the oil; the cooler the climate, the more unsaturated will be the glycerides. Natural phenomena of growth and metabolism play decisive roles in determining the chemical nature of the oil as evidenced by the even number of carbon atoms in the fatty acids which make up the natural glycerides, and also by the position of the first double bond between the 9-10 carbon atoms of these acids. Synthetic processes of formation can easily be conceived, but their direct application to natural processes is questionable. One of the most widely proposed mechanisms is the following:

(a) Formation of fatty acids:

(1) $CO_2 + H_2O \rightarrow HCHO \rightarrow C_6H_{12}O_6$ (polymerization)

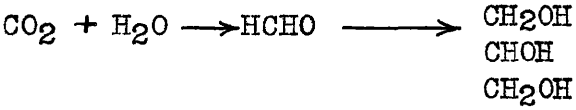
(2) 

$$\begin{matrix}CH_2OH\\CHOH\\CHOH\\CHOH\\CHOH\\CHO\end{matrix}\longrightarrow\begin{matrix}CH_2OH\\CHOH\\CHO\end{matrix}\longrightarrow\begin{matrix}CH_3\\CHOH\\COOH\end{matrix}\longrightarrow\begin{matrix}CH_3\\CHO\end{matrix}+HCOOH$$

glyceryl aldehyde lactic acid

(3) $2\ \begin{matrix}CH_3\\CHO\end{matrix}\xrightarrow[\text{condensation}]{\text{aldol}} CH_3CHOHCH_2CHO$, which is oxidized and reduced ⟶ $CH_3CH_2CH_2COOH$, or further in the same way to stearic acid.

(b) Formation of Glycerol:



$$CO_2 + H_2O \longrightarrow HCHO \longrightarrow \begin{matrix}CH_2OH\\CHOH\\CH_2OH\end{matrix}$$

(d) Formation of fat or oil:

glycerol + fatty acid + lipase ⟶ fat or oil

Linseed oil is obtained from the seed of the flax plant. Domestic seed is usually known as flaxseed, and the imported seed as linseed. The flax plant has several remarkable characteristics. If it is grown for its oil content, it has little use as a fiber, and conversely, if it is grown for its fiber, its oil content is poor. Secondly, its production is possible over wide climatic conditions. Among other places, it is grown in North Dakota, Northern Russia, Argentina, Southern Russia, and India. Flax is liable to attack by a fungus which gets into the soil and destroys the root of the plant. For this reason, the flax plant has a reputation of poisoning the soil, and replanting has been discredited. According to Bolley (13) this poisoning is due to bacteria and can be avoided, largely, by using formaldehyde disinfected seed, by avoiding contaminated seed, or by using seed, which has been made immune by a selective process of growth.

Oil seed from different localities varies in many respects. South American seed is clean, the grains are large and plump, but the percentage of oil is rather low, usually ranging between 36 and 39 per cent. The iodine number of the oil is often around 170 and has been reported lower. The oil is slow to dry and never produces as hard a film as oil derived from North American seed. This latter oil-seed averages 36.5-40.0 per cent oil, which has an iodine number between 178-190 and dries to a hard film. Calcutta and Bombay seed averages 37.50-42.0 per cent oil. Calcutta oil has a lower iodine number than North American, but it is remarkable in its resistance to acid, not showing much free fatty acid even after acid-bleaching.

There are three methods of extracting the oil from the seed:

1. The old method of grinding, heating, and pressing by hydraulic pressure.
2. The Anderson expeller mill.
3. The extraction process.

Vegetable oils have, from the earliest times, been extracted from the oil-bearing substance by use of a press. One of the earliest recordings is that of Aetius in the fifth century. He gave directions for making walnut oil, saying that it -

> "is prepared like that of almonds, either by pounding or pressing the nuts, or by throwing them, after they have been bruised, into boiling water. The medicinal uses are the same, but it has a use besides these, being employed by gilders or encaustic painters, for it dries and preserves gildings or encaustic paintings for a long time."

From the laboratory of Leonardo da Vinci, the greatest painter of the fifteenth and sixteenth centuries, comes this recipe for walnut oil preparation:

> "The nuts are covered with a sort of husk or skin, which, if you do not remove when you make the oil, the coloring matter of the husk or skin will rise to the surface of your painting and cause it to change. Select the finest nuts, take off the shells, put them into a glass vessel of clean water to soften until you can remove the skin, change the water, and put the nuts into fresh water seven or eight times, until it ceases to be turbid. After some time the nuts will dissolve and become almost like milk. Put them into a shallow open vessel in the air and you will soon see the oil rise to the surface. To remove it in a pure and clean state, take pieces of cotton, like those used for the wicks of lamps, let one end rest in the oil and the other drop into a vase or bottle, which is to be placed about the width of two fingers below the dish containing the oil. By degrees the oil will filter itself, and will drop quite clear and limpid into the bottle, and the lees will remain behind. All oils are of themselves quite limpid, but they change color from the manner in which they are extracted."

In the numerous recipes of the middle ages there are many which show how common was the belief that water was essential to the separation or purification of oil.

Present day oil is prepared by grinding the flaxseeds to meal on steel roller mills at 90°C., moistening with steam, and subjecting the mash to high pressure in a hydraulic press. Some protein and carbohydrate materials and other substances are emulsified or otherwise carried over with the oil. The residue after pressing is left in the form of a cake, known as linseed oil cake. The temperature of the meal, as it leaves the heaters, varies considerably in practice. Often the first pressing is run in the cold, the product thereby obtained being of the highest quality. Succeeding runs are done at higher temperatures, and the final run,obtained by heating to a still higher temperature, is known as "foots". The oil left in the cake runs from 5.5 to 6.5 per cent.

In the Anderson expeller mill method, the meal is heated only slightly and is forced by a screw through a conical grating. The oil comes through the grating, and the meal, formed into cuplike scales, comes out the end of the expeller. The oil left in the scales sometimes exceeds eight per cent.

The extraction process, largely a European development, requires that the seed is not crushed too fine, because of difficulties with channeling and later solvent recovery. After grinding, the seed is leached with light petroleum naphtha, which dissolves the oil and leaves a meal containing less than 4 per cent oil. The naphtha is recovered by distillation and is returned to the system. This process has the additional advantages of simplicity and low personnel overhead. Its chief disadvantage is the fire risk, accompanying the use of the solvents.

II. The Refining Of Raw Oil

Linseed oil direct from the presses contains foreign matter from the seed (foots), protein and carbohydrate mucilage (break), free fatty acids, coloring matter, water, etc. According to the future use of the oil, some or all of these impurities must be removed.

The suspended meal particles are largely removed by cloth filters, followed by tanking and final filtration through paper before shipment. A common laboratory method consists of mixing oil with a large amount of water, boiling the water, replacing the evaporated water, and so on for two to three days. Then the mixture is allowed to settle and the oil is poured off. The oil in the water emulsion is freed by adding salt, and is completely dried by using an anhydrous salt such as white vitriol (Z_nSO_4).

The break is removed by heating the oil rapidly to about 400°F. At this point the oil thickens and becomes filled with a gelatinous material. This can be filtered out and washed with petroleum ether. From analysis it is found to be composed largely of phosphates in combination with non-oleaginous organic matter. Obviously acid or alkali treatments will also remove this mucilage.

Linseed oil is sometimes refined for special use in different industries. This refining method may consist of acid treatment, alkali treatment, refrigeration, bleaching with fullers earth, sunlight, benzoyl peroxide, chlorine or ozone, and other operations.

In the acid treatment, strong sulfuric acid, equal to about one per cent by weight of the oil, is slowly added to the oil and thoroughly agitated either mechanically or by air. When the oil turns muddy green it is allowed to settle overnight. Then the clear oil is drawn off, some water is added, and the whole mass agitated with steam. After settling, these operations may be repeated if necessary. Finally the oil is stored to allow the remaining water to settle out. The clear oil drawn off for use has increased amounts of free fatty acids but it is free from mucilaginous matter and some of the coloring matter.

The alkali process usually consists in treating the oil with caustic soda to saponify and remove the free fatty acids, and neutralize the oil.

Bleaching oils by direct sunlight has not changed much in the last two thousand years. In 100 B.C. Dioscorides described a method of bleaching oils as follows:

> "Oil is bleached in this manner: Select it of light color, and not more than a year old,

> pour about five gallons into a new earthenware vessel of an open form, place it in the sun, and daily at noon dip and pour back the oil with a ladle, beating up its surface, till by constant agitation it is thoroughly mixed and made to foam. It is thus to be treated for several days. If it be not sufficiently bleached, place it again in the sun, repeating the above operation until it becomes colorless."

Ozone bleaching is effective but increases acidity and specific gravity, and decreases the iodine value and drying time of the oil. The oil is rendered less suitable for grinding with pigments and darkens when heated above 450°F.

Fullers earth may be used with or without alkali treatment. The more common method uses 5 per cent fullers earth, which is later removed from the finished oil by filter-pressing. The resulting cake is either steamed in the press to recover all of the oil or is broken up and added to ordinary oil cake to be sold.

A more costly and difficult bleach can be produced by heating with dichromate, manganese dioxide and hydrochloric acid to 100°F., agitating for about one-half hour, allowing the clear oil to settle in clean tanks for several weeks and drawing off the refined product.

Outside of its use in paints, linseed oil has its principal use in the preparation of varnishes, lithographic oils, linoleum and artificial leather. For these particular uses as well as for special paints, linseed oil must be further processed by means of heat and/or air.

III. The Processing Of Raw Or Refined Oil

Stand oil or lithographic oil is made from refined linseed oil by heating it somewhat above 600°F. for three days or less. This is a polymerized oil which contains no driers. The best grades are very viscous and colored about the same as the original oil. Such oil may be thinned with turpentine or benzene, driers may be added if desired, and it dries with a good, permanent gloss to a hard film, less elastic than ordinary oil. It is used in making printing inks, and is mixed with prepared tung oil as an ingredient in paints and varnishes.

Boiled oil is usually raw oil, well settled and filtered, which has been heated with driers, such as the oxides of lead or manganese. The original method was to heat at 450° to 500°F. from five to six hours with the addition of about one percent each of litharge, red lead, and manganese dioxide. Of course, the linseed oil does not actually boil, but it does undergo destructive distillation and heat polymerization. In modern practice, a concentrated boiled oil, known as "crushers drier", is first prepared. This is then mixed with about sixteen parts of raw oil and reheated to 350°F. to complete solution. The commercial product contains about 0.2 per cent lead protoxide and 0.05 per cent manganese oxide. The oil dries with a pronounced gloss and makes a fairly hard film overnight.

The use of driers, especially litharge, is probably of great antiquity. As far back as the second century, Galen said that litharge and white lead are drying in their nature. Marcellus, in the fourth century gave directions to -

> "put some oil in a new vessel and put it over a moderate fire, then add well-ground litharge, sprinkling it little by little with the hand. Stir it constantly until the oil begins to thicken."

Somewhat later, Eraclius wrote of white lead as a drier for linseed oil and gave the following directions:

> "Put a moderate quantity of lime into oil and heat it, continually skimming it, add white lead to it, according to the quantity of oil, and put it in the sun for a month or more, stirring it frequently. And know that the longer it remains in the sun the better it will be. Then strain it and distemper the colors with it."

Manganese compounds were first mentioned in a letter of Joseph Petitot written in 1644, which stated that the ordinary drier for drying oils was umber. On purely theoretical grounds, Michael Faraday recommended the use of manganese compounds as oil driers.

A third important processed oil is blown oil. In this method the oil is thickened and oxidized by blowing cold air through oil which has been heated to 250°F. Driers may be added below 160°F. if desired. Since the temperature tends to rise during the process, provision must be made for cooling the oil. Foaming also causes some difficulty but mechanical stirrers or air jets are effective in controlling this tendency.

Another method, which is sometimes used, consists in heating the air to 400°F. in a superheater coil and blowing this air through cold or preheated oil. This process produces an oil which dries better and has less color than oil blown with cold air. However, it has the disadvantage of completely polymerizing into a jelly if the blowing is not carefully controlled.

Blown oil has advantages in that it wets pigments readily and produces better flowing properties in varnishes. Obviously it will dry faster than raw linseed oil because of its preliminary oxidation.

If linseed oil is completely blown to a gel, a very insoluble substance, linoxyn, is produced. This oxidized oil product resists ordinary solvents but is easily attacked by strong acids and by strong or weak alkalis. Linoxyn finds extensive use in the preparation of linoleum and related materials.

IV. Other Fatty Oils

Tung oil or chinawood oil is unique among the fatty oils. It possesses both a high and an unusual type of unsaturation; it readily isomerizes to a white, crystalline compound; it polymerizes in a different manner and degree; it dries rapidly to a wrinkled film unless it is previously carefully heat treated. The oil is obtained from the seeds (nuts) of a tree indigenous to China and Japan. The seeds are usually roasted, crushed and pressed. Cold pressed oil is pale yellow, and is known as "white tung oil." Hot pressed oil is dark in color, and is called "black tung oil." The fresh oil is usually cloudy and has an odor resembling that of bacon grease. The ability of tung oil to polymerize and/or dry rapidly and the excellent water resistance of its films has led to its extensive use in varnishes and linoleum. When incorporated with rosin or with ester gum (glycerol ester of rosin), and suitably thinned, a water-resistant varnish is obtained. When heated to 230°C. or over, the oil coagulates to a transparent solid which is elastic under compression, and this product may be used as a rubber substitute or factis. A more recent use has developed with the perfection of synthetic resin varnishes and brake lining saturants. Many of these synthetic resins are soluble in tung oil but will not dissolve in any other fatty oil.

Perilla oil occurs to the extent of 36 per cent in the nuts of a plant indigenous to East India, Manchuria and Japan. It has the highest iodine value of any known oil but its drying qualities are inferior to linseed oil because it forms drops when spread on a hard surface. When blown, it bleaches and bodies rapidly. The boiled oil dries rapidly to very hard films and finds favorable use in paints and linoleum.

Other vegetable drying oils are hempseed, poppyseed, sunflower, and tobacco seed oil. These oils find limited application in varnishes, painters' colors and soaps.

Among the semi-drying vegetable oils, soyabean oil is probably of most importance to the protective coating worker. Four varieties of the bean are known in China, namely, white, yellow, green and black. The oil is obtained by methods quite similar to those described for linseed oil extraction. The expressed oil is somewhat darker than that obtained by solvent extraction. The oil cake obtained by pressure methods is used by the Chinese as food. Elsewhere it finds use as cattle food or fertilizer. Refining of the oil follows procedures similar to those for cottonseed oil, which will be discussed shortly. Since the expressed oil is practically neutral, it may be used directly for the manufacture of soap. For edible purposes it is usually bleached first with fullers earth, but for technical purposes the oil may be chemically bleached. Soyabean oil is said to add flow to varnish making and to increase the wetting power of pigments. To a limited extent it is used in paints and varnishes, particularly if the prices of linseed and tung oils are unduly high.

Cottonseed oil is also a semi-drying vegetable oil. The oil as it comes from the press varies in color from a yellowish brown to a dark ruby, depending upon the nature and condition of the seed from which the oil has been expressed. The raw oil contains mucilage, mealy matter, coloring and tarry material. Filtration, using filter aids such as diatomaceous earth or activated carbon, is usually followed by careful refining to produce an oil which is widely used as salad oil, in the manufacture of butter and lard substitutes, and as an adulterant for the more expensive edible oils such as olive oil. One of its most important uses is in the manufacture of toilet and laundry soaps.

Rape oil, when properly refined is an edible oil; the more inferior products are used as lubricants and illuminants. Rape oil, as well as cotton oil, can be converted into rubber substitutes by treatment with sulfur chloride or by heating with sulfur. Rape oil is also blown with air to produce thickened products.

Castor oil is unique among the semi-drying oils because it possesses unsaturated hydroxylated glycerides. The cold pressed oil is used for medicinal purposes. The lower grades are used in manufacturing operations, such as leather dressings, and in the sulfonated condition is known as "Turkey red oil" or "Monopol oil." Due to its high viscosity, castor oil is used in lubricants, particularly in airplane engines. Sulfur unites readily with it to produce a rubber-like compound. When hydrogenated, the oil yields a very hard product which has been used in the manufacture of insulating materials.

Other semi-drying vegetable oils include pumpkin seed oil, corn oil, croton oil and sesame oil.

The non-drying vegetable oils do not become gummy when exposed to air at ordinary temperature, but thicken when heated. This class includes olive oil, peanut oil, almond oil and peach kernel oil. They are mainly used as edible oils and as soap raw materials.

Animal oils are obtained by heating the fatty matter with live or dry steam in open kettles or closed digesters. One of the most modern processes consists in heating the stock with water, at a pressure sufficiently high to cause a complete separation, but not high enough to decompose the stock. The rendered product is then filtered and allowed to stand, after which the oil is drawn off. The remaining liquid portion may be reworked or concentrated for use as glue stock. The solid matter is usually dried and used as fertilizer.

Fish oils are drying oils of the marine animal classification. The most important of these is menhaden oil, which is prepared from the body of a fish resembling herring, but somewhat larger. The oil is extracted by a continuous process using live steam and long iron cylinders. The crude product varies in color from light amber to dark brown. For many uses the oil is bleached with fullers earth or alkali, or blown with air at 110°F., which increases its color and acidity and considerably decreases its odor. Other methods used to deodorize fish oils are: (1) hydrogenation, (2) pine oil, (3) heating in the presence of driers, and (4) steam jet in the presence of alkali. Formerly menhaden oil was used principally as an illuminant and in currying leather, and only moderately as a paint vehicle, lubricant and soap raw material. Today, however, large quantities are used in paints and varnishes although the oil never dries permanently hard and has a tendency to become soft in warm, moist weather. It is also used in the tempering of steel and the manufacture of oilcloth, linoleum and printing inks. The substitution of fish oil for linseed oil in the preparation of patent leather affords a coating which is less liable to crack, even though the coating is somewhat less glossy. Sardine oil and salmon oil are similar to menhaden oil, but find very limited applications.

Liver oils are characterized by the large amount of cholesterol and biliary substances present in them. They include cod liver oil, shark liver oil and haddock liver oil. Although they have fairly high unsaturation, their only important use is for medicinal purposes.

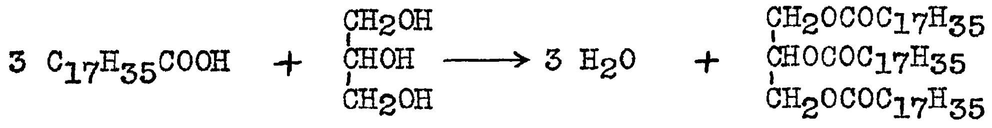
Blubber oils are semi-drying oils and include seal oil, whale oil and porpoise oil.

Terrestrial animal oils, such as neats foot oil and tallow oil are strictly non-drying oils. Their main applications are as lubricating and leather oils.

COMPONENTS OF FATTY OILS

I. Fatty Acids

The composition of fatty oils was first placed on a scientific basis by Chevreul, who, in the early part of the last century, showed that the treatment of a fat with an alkali resulted in decomposition forming glycerine, which remained free in the lye, and fatty acids, which combined with the alkali to form soaps. Subsequently Berthelot confirmed these results and succeeded in producing the glycerides by heating the fatty acids with glycerine under pressure in sealed tubes. Among others he synthesized tristearin:-



$$3\ C_{17}H_{35}COOH + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \longrightarrow 3\ H_2O + \begin{array}{l} CH_2OCOC_{17}H_{35} \\ | \\ CHOCOC_{17}H_{35} \\ | \\ CH_2OCOC_{17}H_{35} \end{array}$$

Most of the fatty acid content of oils is present as esters but a definite small percentage of free acid always exists or is produced from pressing, storage and refining operations. Up to the present time no accurate, rapid method of analysis has been developed. Selective precipitation of soaps, selective halogenating reactions and other attempts have been of doubtful accuracy and in most cases the procedures have been unduly tedious.

The existence of stearic, oleic, linoleic and linolenic acids in linseed oil was first shown in 1886 by Hazura (23). On the basis of the bromination and oxidation of the fluid acids, Hazura concluded that they contained 5 per cent oleic, 15 per cent linoleic and 65 per cent linolenic acids. However, the calculated iodine number is much larger than the actual iodine number of the oil.

Hahner and Mitchell (24) studied the bromine derivatives of the linseed fatty acids and obtained 20-30 per cent of the acids as a solid hexabromide (M.P.180-181°C.). Linolenic acid of iodine number 241.8 was obtained upon debromination and only a small part of the crystalline hexabromide was formed upon rebromination.

Using similar bromometric methods, Fokin (25) concludes that linseed oil contains 22-25 per cent linolenic acid and 5 per cent of solid acids.

Ruhemann and Browning (26) suggest the addition reaction of piperidine to double bonds as a quantitative analytical attack.

From oxidation experiments, Fahrion (27) concluded that there was 15-20 per cent of oleic acid and from 8 to 9 per cent of saturated acids. Using these values and the iodine number, he calculated 25-35 per cent linoleic and 35-45 per cent linolenic acids. His hexabromide yield was only equivalent to 11 per cent linolenic acid, from which he concluded the remainder must be isolinolenic acid. Later, however, he states that the isomer arises through bromination and is not an original component of the oil.

Erdmann, Bedford and Raspe (28) separated the saturated and oleic acids by the barium soap method of Farnsteiner. After changing the mixture of linoleic and linolenic acids so obtained into their ethyl esters and determining the hydrogen number, they calculated that there was 22 per cent linolenic acid in linseed oil. Since their hexabromide determination indicated only 16-17 per cent linolenic acid, they concluded the remainder was present as β-linolenic. Improved methods of analysis have indicated that 20-22 per cent α-linolenic acid is present, which seems to confirm Erdmann's hydrogen number. However, if the iodine number is calculated, his results are much lower than recorded iodine values of the mixed linoleic and linolenic acids of linseed oil (cf. Kaufmann and Keller (29)). All available data seems to indicate that the barium soap separation of saturated and oleic acids is not quantitative.

Coffey (30) in 1921, based his work on the action of oxygen upon the unsaturated acids of the oil. His method was essentially that of von Genthe (31) in which the oxygen is absorbed by the linseed oil at 100° C. The consumption of oxygen is measured and the oxidation products are estimated. Coffey obtained the α- and β- linolenic acids by bromination and subsequent debromination of the pure, crystalline hexabromide, which melted at 185°C. He estimated the amount of α-linolenic acid from the hexabromide number and found that the only constituent of linseed liquid acids evolving CO_2 upon oxidation was the α- linolenic acid. He determined the saturated acids by freezing in petroleum ether to -18°C. In the mixture of liquid acids he determined the percentage linolenic acid from the amount of CO_2 formed during oxidation. At the same time, he showed that oleic acid was not oxidized under his conditions. Therefore the total oxygen consumption corrected for the per cent absorbed by the linolenic acid gives a measure of the linoleic acid percentage. The iodine number can be used finally to calculate the quantity of oleic acid in the mixture. Coffey's results are as follows:

8.1 % saturated acids and unsaponifiables
4.5 % glycerine
5.0 % oleic acid
48.5 % linoleic acid
34.1 % linolenic acid

He agrees with Erdmann (28) that the solid hexabromide is obtained only from α-linolenic acid and his results indicate 22 per cent linolenic acid. He concludes that the remainder (12.1 per cent) must be β-linolenic acid.

Several years later, Eibner (32) published his work on the separation of the unsaturated constituents of linseed oils by bromination and debromination processes. After the estimation and separation of the saturated acids, he prepared the hexabromide and tetrabromides of α-linolenic and α-linoleic acids. The filtrate from this preparation was debrominated and rebrominated, whereupon more solid hexabromide was obtained. Evidently some of the original liquid hexabromide must have isomerized. Eibner's results for a Dutch linseed oil are:

α-linolenic	20.1%
iso-linolenic	2.7%
α-linoleic	17.0%
β-linoleic	41.8%
oleic	4.5%
saturated acids	8.3%
glycerine	4.1%
unsaponifiable matter	1.0%

However, it must be emphasized that only the α-linolenic, α-linoleic, saturated acids, unsaponifiable matter and glycerine were experimentally determined, the remainder were calculated. Eibner admits the doubtful value of iso-linolenic from which the β-linoleic and oleic acid contents are calculated. Furthermore, his method gives widely varying results with different oils (e.g. a sample of Calcutta oil gave 17.6 per cent oleic acid and 22.8 per cent iso-linolenic acid).

The possible use of Wijs reagent as an analytical aid was studied by Cerdeiras (33) who found that the rate of reaction was too rapid for differentiation.

Kaufmann (34) described the use of bromine in the analysis of oils. He showed the effect of solvents on the reactivity of the bromine.

Shortly thereafter, Vaubel (35) found three bromine values for fats and oils, merely by varying the time. The first of these corresponds to immediate saturation, the second is after two hours, and the third after two days. From experimental results, he showed that the first addition saturated the 9-10 bond in all acids and the 12-13 bond in linolin and polymerized linolenin (polymerized at the 15-16 bond). The second addition saturates the 12-13 and 15-16 bonds of linolenin, and the third addition saturates the 15-16 bond of polymerized linolenin. He gives data to show how to relate these bromine values to the composition of the drying oil. A similar concept using the periodine value has been introduced by Margosches (36).

Some support to these ideas is furnished by the work of Smull and Knauss (37), who used dry Br_2-CCl_4 reagent to lessen the possibilities of substitution. From their results they conclude that the rate of bromination of oleic, linoleic and linolenic acids is in inverse ratio to the number of double bonds.

Kaufmann (38) made use of the selective action of thiocyanogen as a means of analysis. The value of this reagent lies in the fact that it acts as a mild halogenating agent, saturating only one of the two double bonds in linoleic and eleostearic acids, and only two of the three double bonds in linolenic acid, while it completely saturates oleic acid. In conjunction with iodine value, a proximate oil analysis can be made. Greater accuracy can be obtained if hexabromide values, saponification values, etc., are obtained. However, this makes the method exceedingly tedious. A detailed description of this type of analysis is given by Hoback (39). Difficulties are encountered when the oil contains oxidized or hydroxylated acids, but corrections can be made which somewhat mitigate these errors.

Other investigators, notably Gardner, Jamieson (42), Gay (44) and Yamaguchi (45), have attempted analysis based on thiocyanogen values. Gay is of the opinion that the reagent is unreliable and useless, but Yamaguchi opines that the method is far superior to the bromination methods.

Van der Veen and Van Loon (43) conducted studies on both bromination and thiocyanogen methods. Their results show that both plans of attack lead to unreliable results.

Recently, Heiberger (46) has shown that the selective adsorption of fatty acids or their soaps on numerous solid adsorbents is not sufficiently so to enable quantitative separations to be made.

The "elaiden reaction" has also been proposed as a means to estimate triolein, but in the opinion of Griffiths and Hilditch (47), this is not likely. The process is an equilibrium reaction and the final product has the same composition no matter whether the cis or trans ethanoid acid is isomerized. In a later article (48), the same investigators develop a procedure using the oleic-elaidic acid transformation as an aid in analyzing mixtures of oleic, linoleic and linolenic acids.

Dawson (49) proposed a physical method for estimating mixtures of isomers and related substances. He used plots of physical properties, such as density, viscosity, conductivity, refractivity, specific heat, surface tension, etc., against composition to show the usefulness of his method.

Täufel and Rusch (50) studied the indirect analysis of three component systems, particularly fatty acid mixtures. Their method involved a knowledge of the iodine value and neutralization value of the mixture.

Solvent fractionation seems to be applicable to some extent. Oils and fats (51) may be fractionated by using two or more solvents of different volatility. Andrè (52) applied fractional diffusion to the proximate analysis of lipides and mixtures of hydrocarbons of high molecular weight.

X-ray diffraction studies and molecular film measurements would probably yield valuable results concerning the quantitative analysis of fatty oils, but at present these studies are still in the embryo stage of development.

The analysis of other oils, in general, follows similar procedures. Long (53) has tabulated the best results on the average composition of a number of oils. These are listed for future reference on the following page. Van Loon (40) and Kaufmann (41) give excellent resumes of the work on chinawood oil and perilla oil respectively.

II. Unsaponifiable matter

Alcohol and hydrocarbon type compounds have been detected but no quantitative studies have been made on this fraction of raw oil.

Cutter (54) is of the opinion that the main

TABLE A

COMPARATIVE COMPOSITIONS OF TYPICAL FATS AND OILS

ACIDS	Double Bonds	Linseed Oil		Chinawood Oil	Perilla Oil	Soybean Oil
Stearic	0	5.2	5.2	1.2	7.2	4.2
Oleic	1	14.7	9.9	13.6	3.7	32.0
Linoleic	2	39.4	40.7		41.9	49.3
Linolenic	3	35.7	39.2		41.7	2.2
Eleostearic	3			72.8		
Palmitic	0			3.7		6.5
Arachidic	0					0.7
Glyceryl Radical		4.6	4.6	4.4	4.6	4.6
Iodine No.		182.9	190.7	(217 real (165 Wijs	204	124-143

ACIDS	Double Bonds	Walnut Oil	Fish Oil (Menhaden)	Castor Oil	Olive Oil
Stearic	0	0.9		2.5	2.3
Oleic	1	16.9	24	7.0	84
Linoleic	2	69.7	19	3.5	4.6
Linolenic	3	3.1			
Clupanodonic	4		17.2		
Ricinoleic	1			80.0	
Palmitic	0	4.4	10.5		6.9
Myristic	0	0.01	7.7		trace
Palmitoleic	1		16.3		
Glyceryl Radical		4.6	4.6	4.6	4.8
Iodine No.		132-159	130-160	80-90	77-95

FORMULAS OF ACIDS

Stearic	$CH_3(CH_2)_{16}COOH$
Oleic	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
Linoleic	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$
Linolenic	$CH_3(CH_2)CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$
Eleostearic	$CH_3(CH_2)_3CH=CH-CH=CH-CH=CH(CH_2)_7COOH$
Clupanodonic	$CH_3(CH_2)CH=CHCH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_4COOH$
Ricinoleic	$CH_3(CH_2)_5CHOHCH_2CH=CH(CH_2)_7COOH$
Palmitic	$CH_3(CH_2)_{14}COOH$
Myristic	$CH_3(CH_2)_{12}COOH$
Arachidic	$CH_3(CH_2)_{18}COOH$
Palmitoleic	$CH_3(CH_2)_7CH=CH(CH_2)_5COOH$

constituent is a high molecular weight alcohol. He cites the work of Jacobson (55), who isolated a crystalline substance containing some ceryl alcohol.

By means of qualitative tests, Salzenberg (56) detected cholesterol and sitosterol.

The unsaponifiable matter in sheanut fat was analyzed (57) recently. The hydrocarbons, illipene and β -amyrin, and an alcohol, lupeol ($C_{30}H_{50}O$), were detected.

Toyama and Isikawa (58) detected the presence of saturated and unsaturated alcohols and hydrocarbons in the unsaponifiable matter of whale oil.

III. Mucilage

This fraction of raw oil results from carbohydrous material in the seed. A portion of this is associated with oil and another portion is associated with water. On standing, this latter portion settles out. Heating with or without water precipitates most of the mucilaginous matter as the so-called "foots" of the oil. Most workers are of the opinion that phosphatides and other combinations of phosphates with non-oleoginous matter are the main constituents of the oil mucilage.

Cohen (59) isolated cephalin from the aqueous extract of linseed oil. Shafranovskaya (60) hydrated linseed oil and obtained a sediment which contained 20 per cent phosphatides, 16 per cent albumins, 7.5 per cent hydrocarbons (polysaccharides) and 12.9 per cent mineral substances.

IV. Coloring Matter

Very little is known concerning the actual color-bearing compounds in fatty oils. Cutter (54) states that there are at least two kinds of coloring matter, one of which is easily removed by ordinary refining. Cohen (59) indicates that chlorophyll, xanthophyll and carotenoids are present in raw oil as colored complexes which exert strong anti-oxidant activity.

V. Glyceride Combinations

Two groups of investigators, using bromination and fractional crystallization technique, have contributed most of our present knowledge of the linseed oil glycerides.

Suzuki and Yokohama (61) have identified linolenye-dilinolyl glyceride, two types of dilinolenyl-linoyl glyceride, and dilinolyl-olyl glyceride.

Using similar methods, Eibner (62) and Davidson (63) isolated dilinolenyl-linoyl and dilinoyl-olyl glycerides. No simple glycerides were ever detected, a fact which accounts for the independence of drying power and percentage oleic acid. Up to 20 per cent oleic acid, the drying is not greatly affected as long as sufficient other acids are present so that only mono-olyl glycerides can be formed.

Collins and Hilditch (64) have studied the regularities in glyceride structure of vegetable seed fats. The fatty acids, mostly saturated, are distributed as evenly as possible; simple triglycerides may occur if one acid is present in very large percentage. They further conclude that pericarp fats, animal body fats, milk fats and synthetic triglycerides have different glyceride structures.

Hilditch (65) showed that all the acids tend to distribute themselves evenly among the glycerides. He believes that a single acid must be greater than 25 per cent of the total amount of acids before more than a monoglyceride of that acid can form. However, the addition of non-oxidizing acids will certainly alter the final product; particular combinations of acids are without doubt preferable.

Tung oil glycerides have also been investigated. Boeseken (66) states that the constituent glycerides are still doubtful but he believes that α-eleostearin is the main constituent. Boeseken and

Ravenswaay (67) studied hydrogenation data and deduced that tung oil contains 90 per cent eleostearic glyceride.

Kaufmann (68) using his thiocyanogen method calculates that there is 78-87 per cent eleostearic glyceride present.

ISOMERISM

All fatty oils and fatty acids have a large number of isomers, which may account for the differences in behavior of oils which have the same composition. Both structural and position isomers are possible. Since the main acids present in oils have one or more double bonds, there will be a number of cis-trans isomers as well as isomers with the double bonds in different chain positions.

Theoretically stereoisomers exist wherever a double bond is found if the groups attached to the carbon atoms are unsymmetrical. Oleic acid has an isomer-elaidic acid. Treatment with a trace of nitrous acid converts the liquid oleic acid, m.14°C., into its solid trans-isomer, elaidic acid, m.51°C. Their structural identity is easily proved by hydrogenation or by vigorous oxidation. Theoretically, many isomers may exist in a drying oil; linoleic acid has four stereoisomers and linolenic acid has eight. There is only the indirect evidence that these isomers actually exist, but they have been shown to alter reactions rates such as the decomposition of the hexabromides of linolenic acid. Erdmann (69) formed the hexabromide and obtained linolenic acid by debromination with zinc and alcohol. Upon rebromination only about a quarter of the original hexabromide was obtained and exhaustive examination of the acid obtained by debrominating this proved it to be linolenic. He concludes that an isolinolenic was formed on debromination. The acid in linseed oil which yields the solid hexabromide was called α-linolenic, and that prepared by isomerization upon debromination, β -linolenic.

Pigulevscku (70) has obtained solid and liquid isomers of linoleic acid. Other instances of isomeric linoleic and linolenic acids have been mentioned in connection with the analysis of linseed oil. Whitmore (21) states that eleostearic acid has been detected in several stereo forms.

Chain isomerism is probably more important than stereoisomerism because: (1) As the double bond approaches the carboxyl group its reactivity and behavior are changed; (2) When several double bonds are involved, their isomerization may lead to conjugated systems possessing increased reactivity. Of course the presence of these acids as glyceride esters will somewhat modify but will not change the relative degree of reactivity. A brief review of the reactions of unsaturated acids will aid us in interpreting later experimental data.

Acrylic acid, $CH_2 = CH\text{-}COOH$, possesses a mixed conjugated system which modifies both the usual acid reactions and the usual double bond reactions. It gives reactions with unusual ease and adds X from HX in the beta position, contrary to Markownikoff's rule. Reactants like NH_3, HCN, alcohols, sodium malonate, etc., involve 1,4 addition with the H or Na adding to the carbonyl oxygen. Reactants like HOCl, which cannot add to oxygen, yield a mixture of isomers. Acrylic acid polymerizes readily. It splits at the double bond when heated with alkali. As the chain grows through crotonic ($CH_3CH=CHCOOH$) to long chain acids, the tendency to polymerize decreases, but other reactions remain unchanged.

Vinyl acetic acid, $CH_2 = CHCH_2COOH$, is a $\beta - \gamma$ unsaturated acid. It gives the reactions of an olefin and of a carboxyl compound practically independent of each other. However, it adds Br_2 more rapidly than does the $\alpha - \beta$ unsaturated acid. This is easily understood when we consider that bromine will not add to oxygen, a necessity if 1,4 addition is to take place. When treated with dilute acids or alkalis, it changes to crotonic acid. However, the change from an unsubstituted beta-gamma to an alpha-beta unsaturated acid is not reversible, because an alpha H atom is so much more reactive than a gamma H atom, that a beta substituted compound, which can form an olefin by loss of HX, always selects the alpha H atom. this helps to explain the biological "beta oxidation" of fats, which may have some counterpart in certain reactions of drying oils. Beta-gamma acids readily form 6-member ring lactones. Concentrated alkali shifts the double bond to the alpha-beta position and then splits the molecule.

Undecylenic acid, $CH_2 = CH(CH_2)_8 COOH$, and similar acids behave much like typical $\beta - \gamma$ unsaturated acids. Alkali shifts the double bond in a reversible manner unless an $\alpha - \beta$ bond is formed. The $\alpha - \beta$ bond can only change by splitting in the presence of fused alkali.

Oleic acid, $CH_3(CH_2)_7CH = CH(CH_2)_7COOH$, likewise isomerizes and splits when treated with fused alkali. Acetate and palmitate are formed. Oxidation with nitric acid yields all the lower fatty acids from C_{10} to C_2. This indicates a shift in double bond under the influence of acid.

β- vinyl acrylic acid, $CH_2 = CH\text{-}CH = CHCOOH$, is a conjugated, diolefinic acid. Catalytic hydrogenation initiates at the terminal carbon and yields ethyl acrylic acid. Reduction initiates at the carbonyl oxygen as part of the 1,6 conjugated system and yields penten-3-oic acid and some vinyl propionic acid. Vinyl acrylic acid adds Br_2 at the terminal double bond. It polymerizes readily probably through a Diels-Alder reaction of the butadiene system of one molecule with the $\alpha - \beta$ double bond of another.

Sodium malonate adds to the 1,6 conjugated system.

Linoleic acid exists in four possible stereoisomeric forms: trans-trans; trans-cis; cis-cis; and cis-trans. The possibility that the carboxyl group and an olefinic linkage can approach in space, will lead to lactone formation, a process which deactivates the one double linkage.

Linolenic acid, eleostearic acid and other isomeric triolefinic acids are known to have stereoisomers. No direct evidence of a facile isomeric change from unconjugated linolenic to conjugated eleostearic has been found but such isomerization is both conceivable and theoretically sound if the properties of these higher fatty acids are comparable with the simpler type acids.

Armstrong and Hilditch (72) used an oxidation method of ascertaining the position of the ethylenic bond in the oleic acid series. They found definite evidence of the mobility of the double bond in oleic acid.

The diene synthesis has been exploited by Kaufmann (73) and others as a method for determining the active double bonds in drying oils. Kaufmann found the following "diene numbers": (a) triolein = 0; (b) poppyseed oil = 13; (c) cottonseed oil = 5; (d) soya oil = 9; (e) linseed oil = 8.5; and (f) tung oil = 68. Side reactions being excluded, fats must contain active double bonds. Either the unsaponifiable is responsible or else saponification alters the acids so that no conjugated acids are recovered.

Preise (74) applied Meinel's method for the detection of conjugated double bonds to several oils. He obtained positive reactions with raw tung oil and bodied linseed oil. Raw linseed oil and castor oil gave negative results. This indicates that the bodying of linseed oil probably involves isomerization to a conjugated system.

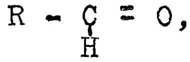
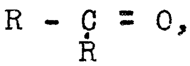
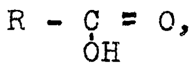
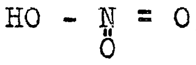
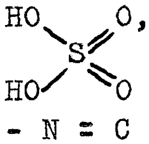
The stereochemistry of glycerides has not been fully investigated. The old viewpoint of an E structure has largely been supplanted by present ideas of a T structure. Molecular models lend support to the idea of T-shaped glycerides.

PROPERTIES OF THE DOUBLE BOND LINKAGE

Since the essential requirement of a drying oil seems to be its unsaturation, a review of the properties of the ethylenic linkage is desirable.

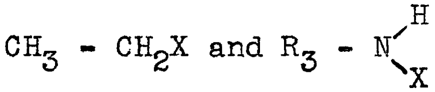
The position of the double bond is a determining factor in the mode of reactivity as evidenced by the discussion on isomerism in the preceding section. These positions have been determined by oxidation, ozonalysis and other methods. Numerous articles have appeared on this subject. Erdmann (69) split the ozonide of linolenic acid and fixed its double bonds at the 9, 12 and 15 carbon atoms. Nunn and Smedley-MacLean (75) oxidized linoleic acid with dilute KM_nO_4 and obtained 11-carboxy, 9, 10 dihydroxy undecanoic acid plus its corresponding lactone acid. By degradation and further examination, they fixed the double bonds at 9-10 and 12-13. Whitmore (21) gives similar results on these and other acids. Oleic acid ozonates to pelargonic aldehyde, $CH_3(CH_2)_7CHO$, and $CHO(CH_2)_7COOH$. Very dilute KM_nO_4 adds two hydroxyl groups to produce 9, 10 dihydroxy stearic acid. More vigorous oxidation gives pelargonic acid and azelaic acid. This evidence fixes the double bond at the 9, 10 carbon atoms. Similarly, the linoleic double bonds are fixed at 9, 10 and 12-13 because alkaline permanganate yields 9,10,12,13 tetrahydroxy stearic acid, and more vigorous oxidation yields caproic acid ($CH_3(CH_2)_4COOH$), oxalic acid, and azelaic acid.

The reactions of these double bonds will be influenced only by the presence of others nearby. The carboxyl group is too distant to exert much influence, except in the cases of certain stereoisomers. The isolated double bonds will have a small influence on each other compared to adjacent or conjugated double bonds. A theoretical study of the ethylenic linkage will give some insight into the reactions of an isolated double bond. Nef (76) has given us a classic research on this problem. The following are excerpts from his paper:

> "The unsaturated bodies can be divided into two large classes: Class "A" containing double and triple bonds between adjacent atoms which can be the same or different from each other, such as ethylene $CH_2 = CH_2$, chlorine $Cl \equiv Cl$, acetylene $CH \equiv CH$, oxygen $O = O$, the aldehyde, ketone, and fatty acid bonds:  $R - \underset{H}{C} = O$,
>
>  $R - \underset{R}{C} = O$,  $R - \underset{OH}{C} = O$, the alkyl cyanide,
>
> $R - C \equiv N$, nitroparaffine  $R - \underset{\overset{\|}{O}}{N} = O$, nitric acid
>
>  $HO - \underset{\overset{\|}{O}}{N} = O$, sulphuric acid  the alkyl
>
> cyanate and thiocyanate, $R - N = C = O$, $R - N = C = S$ and others. The second class, B, consists of those in which the atom can be considered unsaturated. In these classes are to be placed all combinations of an element in which the concerned element-atom does not have the maximum value of its valence. One can assume that the remaining valences of the atom become latent,

that is, simply disappeared or what is more probable is that if two or four valence units are present, they polarize mutually, exactly as the case with a double or triple bond between adjacent carbon atoms. As examples of B, the following classes should be mentioned: ammonia and the amines $= NH_3$,$= NH_2R$, $= NHR_2$, $= NR_3$, methylene $= CH_2$, and its substitution products like $= C = O$, $\overset{=}{=} C = NR$, $= C = NOH$, thio ether $= S = R_2$, alkyl chloride $R - Cl =$, imide $H - N \overset{=}{\underset{=}{}}$, and others.

"If one considers the behavior of a representative of class A, for example, ethylene, in comparison with the behavior of a tertiary amine, class B, then one finds that fundamentally there is no real difference present. For example, both react very easily with acids, H - X, with the formation of addition products according to the general scheme:



$$CH_3 - CH_2X \text{ and } R_3 - N\begin{smallmatrix} H \\ X \end{smallmatrix}$$

"In these reactions the unsaturated bodies absorb the acid forming a saturated system. In similar ways ethylene and thio ether react with the halogenes, very energetically, to form addition products of the general formula: $CH_2X - CH_2X$ or $R_2 = S = X_2$. The sole difference with these reactions is, that with class A there occurs a saturation of two valence units stored up between two adjacent atoms, while with class B, there occurs a saturation of the two valences of one single atom, and by which the atom increases its valence degree.

"No matter whether unsaturated bodies belong to class A or B, the fundamental reason for addition is that the unsaturated substance exerts a dissociating effect on the addition agent. Thus before the bromine molecule can add onto a thio ether, it must be split into bromine atoms: $R_2S + Br - Br \longrightarrow R_2S + Br{-}{-}{-}{-}{-}\ Br \longrightarrow R_2S = Br_2$. Considering things from this standpoint, an unsaturated substance must possess a considerable partial energy in the double or triple bonds or in the unsaturated element atoms. If the valences

> present in the unsaturated bodies do not exist free but are present mutually polarized or latent, the unsaturated substance must first, before it can take up the bromine, change into the nascent state: $CH_2 - CH_2$, or $R_2S =$. For this, naturally, a certain expenditure of energy is required, which, if it is not from another source, must come from that energy existing in the unsaturated substance. Such unsaturated bodies with free valences (in case they are capable of existence) would be much more capable of reacting than the usual unsaturated bodies, just as nascent hydrogen reacts much more energetically than ordinary molecules of hydrogen."

Nef analyzed compounds by the Baeyer tension theory to explain the dissociating power of unsaturated bodies, and continues:

> "Which substances can be dissociated by the unsaturated bodies of class A and B and be taken up by them by addition? Since the behavior of all unsaturated bodies is entirely homogeneous, then it is to be expected that each must combine with all of these substances, or, in case this does not occur, a simple explanation must be found.
>
> "In the following list is given the substances which are usually and very easily taken up by unsaturated bodies by addition action. The line designates the place where the compounds dissociate, that is, become torn apart.
>
> I. Acids, $H - Cl$, $H - Br$, $H - I$, $H - OSO_2OH$, $H - ONO_2$, $H - OCOCH_3$, etc.
>
> II. Derivatives of ammonia (or phosphines and arsines), $H - NH_2$, $H - NHR$, etc.
>
> III. Derivatives of water or sulphuric acid, $H - OH$, $H - OR$, $CH_3CO - OCOCH_3$, etc.
>
> IV. Halogens, $Cl \equiv Cl$, $Br \equiv Br$, $I \equiv I$.
>
> V. Hydrogen, $H - H$.
>
> VI. Chloride acids: $Cl - COCH_3$, $Cl - O - Cl$, $Cl - OC_6H_5$, etc.

VII. Alkyl halides, R - X (where X = Cl, Br, or I).

VIII. Halogen metals or non-metals, Cl - $AlCl_2$, Cl - ZnCl, Cl - $FeCl_2$, etc.

"An addition of the substances under I, II, III occurs very easily with aldehydes, ketones, fatty acids, and cyanides; of I, IV, and VIII with olefines and acetylenes; and addition of chlorine acids, VI, known with some aldehydes, was established with certainty. An addition of alkyl halides, VII, must be assumed since the alkyl group is transposed to the tertiary amines and phosphines as well as to the thio ethers, and in the process, salts of the tetra alkylate ammonium or phosphonium or of tri-alkylate sulphonium bases are formed.

"According to the Baeyer hypothesis the existing tension must be exactly the same in a series of homologous bodies, since these all contain the same unsaturated groups, and therefore the addition of reagents should occur with the same ease in all cases. The bivalent carbon atom existing in carbon dioxide, hydrocyanic acid or its salts, the iso nitriles, and fulminate salts must, in all cases, be considered as acting under the same relation of tension; nevertheless there exists an enormous difference in the ease with which the bivalent carbon atoms existing in those compounds absorb addition reagents.

"With unsaturated bodies, the nature and the mass weight of the molecule, radical, or elementary atom exert an enormous, almost unbelievable, influence on the ease with which the reagents add. I have shown this particularly in the study of the acetoacetic ester and analogous bodies as well as in many methylene combinations. In general one can say that a positive group increases the ease of addition and that a negative group reduces it. The mass of the existing radical or atoms, especially if this mass is big, can exert such an influence that the unsaturated group becomes entirely neutral or that it reacts very difficultly with other substances. Further the radicals and elements which are present each exert a wholly unbelievable influence on the stability on the products of addition of unsaturated bodies of

> those radicals. Thus the factors which contribute to make an unsaturated substance able to exist, as well as the influences which make such an unsaturated body an indifferently reactive body, are various and yet too little is known to allow exact calculation. It is only certain that one cannot compute the ability to react according to angles. The tension hypothesis is also not able to explain why the saturated substances, which are formed through addition reactions out of the unsaturated bodies and in which no tension is present, can be reduced so easily, often spontaneously at usual temperatures, into the unsaturated bodies.
>
> "Concerning the addition processes in unsaturated bodies, specific investigations were made a long time ago. It is well known that an addition occurs much more easily in the presence of light, heat, or electrical influences, and acids, alkalies, water, pulverized metal and so forth.
>
> "Acetylene, for example, does not react at all with chlorine in the absence of light. Although it reacts at a higher temperature with hydrogen, the reaction also occurs at ordinary temperatures, if platinum sponge is present. Hydrogen does not combine with chlorine in the absence of light, although it does so explosively in sunlight. These influences exert a dissociating effect on the unsaturated substances (class A or class B), and also on the reagents (c) which are to be added by them. The bodies, thus transferred into the nascent state, then combine, often with explosive violence."

Kharasch and Dorkis (77) review the various concepts of the ethylenic linkage up to 1929 and present a theory to account for all the experimental facts. They accept the Bohr concept of the atom, and consider that around each atomic center there exists a number of energy levels, and the electrons shared between two carbons may be held at different energy levels. The reference positions are the positions occupied by the eight electrons in methane and in carbon dioxide and they postulate that there are a series of atomic levels through which the electron passes in the transformation from the former to the latter compound, accounting for the heats of combustion. The electron, which is shared, may be held equidistant from either atom, and this equidistant electron may be at lower or higher energy levels, thus differentiating between adjacent carbons of ethane and oxalic acid. In the case of like groups being joined, such as phenyl and phenyl in diphenyl, the electron is at a different level than in ethane and is held equidistant from atomic centers in both cases. This bond, the bond between phenyl and methyl radicals, and the bond between phenyl and carboxyl radicals are different. In the case of unlike radicals being joined, the electron is displaced from the normal and lies closer to one atom than the other. By this concept is explained the experimentally observed differences in heats of combustion and the experimental and predicted values check closely although the differences were small.

The unsaturated compounds differ considerably from the saturated in the heat of combustion. The second pair of electrons shared is displaced from the normal energy levels of one or both atoms, depending upon the polarity of the radicals attached to the carbon atoms.

Their postulates of theory of partial polarity are as follows:

Postulate I - There is a definite polarity at the double bond so that unsaturated derivatives of the ethylene type have definite electrical polarization in at least one part of the molecule.

Postulate II - In the case where radicals attached to the carbon atoms of the double bond are about the same in electronegativity, it is possible that two electroisomers are present.

When such is the case, it is possible that unsymmetrical addition (for example, HX) will give two isomers, depending upon the electroisomers originally present. They do not assume equilibrium between the electroisomers and believe one form can be changed to the other but at the expenditure of energy.

Postulate III - The second pair of electrons constituting the double bond is always held in outer energy levels of one of the carbon atoms and in some closer inner energy levels of the other. The particular level depends upon the nature of the radicals attached to the double bond.

Postulate IV - The relative position of the second pair of valence electrons of the double bond depends upon the nature of the radicals attached to the carbon atoms so that the second pair of valence electrons are always on the carbon atom opposite to that carrying the most electronegative radicals.

Postulate V - Alkyl and aryl radicals are more electronegative than a hydrogen atom. They believe this may not be strictly true but have no data involving the electronegativity of the hydrogen atom, although the radical CH_2X, where X is a strongly electronegative radical, may almost equal the electronegativity of the hydrogen.

Postulate VI - In the formation of an unsaturated derivative from alkyl halide, it is assumed that the halogen is removed, taking with it the pair of valence electrons and the hydrogen drops off to maintain the electrical neutrality of the molecule.

Postulate VII - In case the radicals attached to the carbon atoms of the double bonds are all different, the same principles apply as were developed for compounds in which two radicals of the same type were assumed to be attached to a carbon atom.

They have furnished evidence in support of these postulates. These postulates offer an explanation of the difference in the chemical reactivity of the double bonds in drying oils. Referring to the table of fatty acids, it can be seen that the 15-16 double bond of linolenic acid should be particularly active since the groups attached to the carbon atoms are so unequal in size. By knowing that the electronegativity of the ethyl group is small as compared to that of the rest of the fatty acid or glyceride, predictions can be made about the method of addition of an unsymmetrical reagent. Halogen acid, HX, would then add hydrogen to the carbon nearest the ethyl group. Several facts are in accordance with this hypothesis. The outer bond is more reactive in hydrogenation reactions. Oleic acid rancidity is prevented by the presence of linoleic or linolenic acids which are preferentially oxidized (78).

Bloomfield and Farmer (79) showed that in the addition of HOCl to the compound $RC = C(CH_2)_2COOH$, the carboxyl group did not affect the course of the addition, but when the R was changed from hydrogen to methyl, ethyl or propyl groups, there was an orientation of the chlorine and a marked difference in action.

The evidence presented has indicated that double bonds have considerable differences in polarity as evidenced in the ease of addition when the bonds are located in different positions. In the double bonds of linolenic acid, the 15-16 bond reacts first, the 12-13 bond, which characterizes linoleic acid, reacts next, and the 9-10 bond of oleic acid reacts last. This is true when hydrogen or oxygen are added, but other reagents may change the polarity at one bond sufficiently to affect the course of addition at a second bond.

When the double bonds are conjugated as in $RCH = CH - CH = CHR$ or $R- CH = CH - \overset{O}{\overset{/\!/}{C}} - R$, the reactions do not follow the normal course of addition. A symmetrical reagent usually adds to the 1,4 positions unless it cannot add to oxygen. An unsymmetrical reagent, like $HOCl$ may follow a different course.

Numerous addition reactions have been investigated and can be found catalogued in any standard organic treatise such as Whitmore (21). In the field of drying oils, Overholt (80) and Miller (81) have studied the action of several organic and inorganic reagents on linseed oil. Their results support existing theories of double bond addition, but practical difficulties arise due to the complex nature of their raw material. Further work of this nature on pure esters and acids would lead to a better understanding of the fundamental drying oil reactions.

POLYMERIZATION

I. Introduction

The term "polymer" had been restricted to those like paraldehyde and polystyrene, which have exactly the same percentage composition as the monomers and are formed from them without the addition or subtraction of anything. This viewpoint was held as early as 1833 by Berzelius. More recently Carothers (84) has modified this viewpoint to include the chemical combination of the same or similar molecules to form a new single molecule. The process is any in which similar compounds are heated in the absence of air and added agents to produce addition and/or condensation polymers.

II. Classification

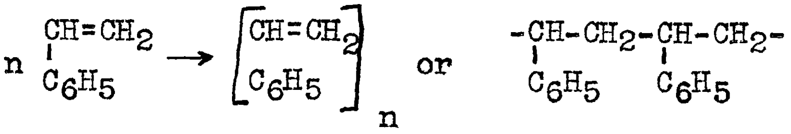
True polymerization reactions lead to polymers which are more saturated than the original reactants and are simple multiples of them.

Condensation reactions lead to polymers which are no longer multiples of the original reactants.

Both classes are characterized by the nature of the reacting materials.

Additive or homopolymerization involves the additive combination of the monomer unit, A.

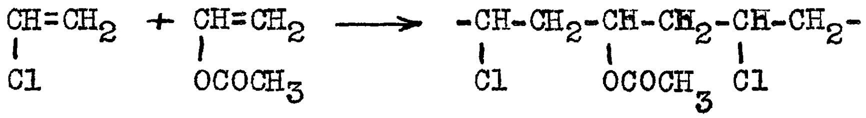
$nA \longrightarrow (A)_n$ or $-A-A-A-$



$$n\,\underset{\mathrm{C_6H_5}}{\underset{|}{\mathrm{CH}}}{=}\mathrm{CH_2} \longrightarrow \left[\underset{\mathrm{C_6H_5}}{\underset{|}{\mathrm{CH}}}{=}\mathrm{CH_2}\right]_n \text{ or } -\underset{\mathrm{C_6H_5}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{C_6H_5}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-$$

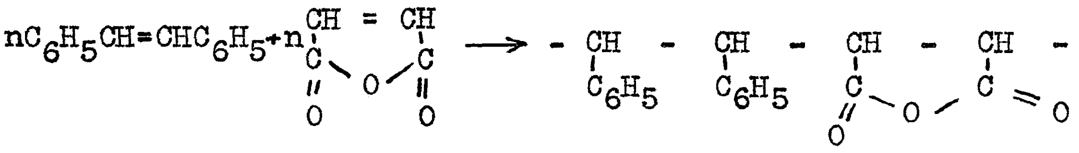
Co-polymerization is the additive combination of two or more substances, each capable of polymerizing alone. The resulting polymer is not necessarily a mixture of polymers.

$nB + nC \longrightarrow (BC)_n$ or $-B-C-B-C-$



$$\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}{=}\mathrm{CH_2} + \underset{\mathrm{OCOCH_3}}{\underset{|}{\mathrm{CH}}}{=}\mathrm{CH_2} \longrightarrow -\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{OCOCH_3}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-$$

Heteropolymerization involves the additive combination of a polymerizable substance and another unsaturated substance which by itself does not readily polymerize.



Simple condensations involve the elimination of simple molecules such as water, alcohol, hydracid or sodium chloride and the condensation of the residues to form polymers. A number of type reactions are possible:

(1) Single condensations -

$Dx + Dx \longrightarrow D - y - D + Z$

$\mathrm{CH_3COOH + CH_3COOH \longrightarrow CH_3CO{-}O{-}COCH_3 + H_2O}$

(2) Multifunctional condensations -

(a) Intramolecular

$$xDx \longrightarrow \underbracket{D\text{-}y} + Z$$

$$HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH \longrightarrow \underbracket{COCH_2CH_2CO\text{-}O} + H_2O$$

(b) Intermolecular

$$xDx \rightarrow x\text{-}D\text{-}y\text{-}(D\text{-}y)_n\text{-}D\text{-}x$$

(c) Inter- and intramolecular

$$xDx \rightarrow x\text{-}(D\text{-}y\text{-}D\text{-}y\text{-}D\text{-}y)_n\text{-}x \rightarrow \underbracket{(D\text{-}y)_m}$$

(d) Multicondensations -

$$x\text{-}D\text{-}y \longrightarrow X\text{-}D\text{-}z\text{-}D\text{-}z\text{-}D\text{-}y \quad \text{or}$$

$$x\text{-}A\text{-}x + y\text{-}B\text{-}y \longrightarrow x\text{-}A\text{-}z\text{-}B\text{-}z\text{-}A\text{-}z\text{-}B\text{-}y$$

The question of when intermolecular condensations take place in preference to intramolecular condensation has been discussed by Carothers (85). He states that when the number of molecules in a unit chain is five, the product is monomeric and cyclic; if the number is six, it may be mono- or polymeric, and if the number is greater than six, it is exclusively polymeric.

A further classification of polymers is based on their "convertibility". Kienle (86) designates heat-convertible polymers as those which become infusible by the action of heat. Resins of this class include the glycerol-polybasic acid resins, alkaline condensed phenol-aldehyde resins, acetylene derivatives and polyolefins.

Heat-nonconvertible polymers are those which remain thermoplastic. Examples are acid condensed phenol-aldehyde resins, vinyl resins, and glycol-polybasic acid resins.

Element-convertible resins are those which become infusible through the action of certain elements such as oxygen or sulfur. This group includes the drying oils, olefin-sulfur resins and glycerol-polybasic acid-drying oil resins.

III. Polymerization vs. Chemical Constitution

The phenomenon of polymerization appears to be closely connected with certain unsaturated groups in the monomer molecules. Broadly speaking, any unsaturated grouping, as exemplified below, acts as a polymerizing factor. The capacity for polymerization -

$-C\equiv C-$ $\quad >C=C<$ $\quad -C\equiv N$ $\quad >C=O$ $\quad >C=N-$ is

determined by these groupings and by external factors such as light, heat, catalysts and pressure.

The tendency to polymerize is greater if all the unsaturation is on one atom, such as -

$>C=C=C<$ $\quad >C=C=O$ $\quad >C=C=N-$

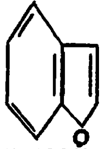
Conjugated systems are even more effective.

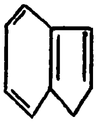
$>C=\underset{|}{C}-\underset{|}{C}=C<$ $\quad >C=\underset{|}{C}-\underset{|}{C}=N-$ $\quad O=\underset{|}{C}-\underset{|}{C}=O$

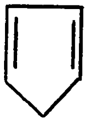
The presence of negative groups is desirable in ethylene derivatives, because of the high degree of polymerization obtained. Vinyl derivatives ($CH_2=CHR$), in which

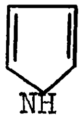
R=COOH, CHO, $COCH_3$, $OCOCH_3$, OCH_2CH_3 or Cl, are very good polymerizing compounds.

When the ethylene group is in a ring, polymers may form, but they are seldom of a high degree. Examples are:-


Cumarone


Indene


Cyclopentadiene


Pyrrole

Negative groups have a reverse effect on the polymerization of carbonyl derivatives. Formaldehyde ($H_2C=O$) readily polymerizes whereas benzaldehyde $\left(\begin{smallmatrix}H\\C_6H_5\end{smallmatrix}\!>C=O\right)$ and phosgene ($Cl_2C=O$) are stable compounds and do not polymerize. However, the substitution of a carbonyl or carboxyl group makes the molecule unstable again, e.g. glyoxylic acid (COOH-CHO), glyoxal (CHO-CHO) and pyruvic aldehyde (CH_3CO-CHO).

If the molecule contains groups which tend to destroy its symmetry, resin formation will be favored. Standinger (87) found that α- methyl styrene $\left(\begin{smallmatrix}C_6H_5\\CH_3\end{smallmatrix}\!>C=CH_2\right)$ polymerizes to an octamer, whereas β- methyl styrene yields only the dimer. He also found that asymmetric $CH_2=CCl_2$ polymerizes much more readily than symmetrical ClHC=CHCl(88). Vorländer (89) has noticed that para substitution in the benzene nucleus tends to give rise to the liquid crystal or mesomorphic state of matter. The predominantly one-dimensional state is one of the most important factors for the formation and cohesion of anisotropic crystals because the linear molecule has the greatest stability with the closest possible packing (90). On the other hand, the formation of supercooled liquids is favored by those influences which prevent the formation of liquid crystals (91). These influences include branched chains, an uneven number of side chains, and ortho- and meta-substitution. He has shown this to be true with various substituted benzene derivatives. The frequent appearance of the unsymmetrical isoprene structure in many natural products lends further support to these theories. According to Scheifele (92), the ideal molecular structure to impart film-forming properties should consist of a nucleus bearing three radiating thread-like groups.

Carothers (84) was the first to introduce the "functionality" concept and relate the polymerization capacity and structure to the nature of the active groups. Functionality refers to the number of active positions in the molecule. In order to form polymeric compounds, the original monomeric molecules must be polyfunctional. The simplest case would be the polymerization of a bifunctional monomer, x-R-y, in which x and y are reactive with each other. Some typical cases are illustrated below:

2,2 $x\text{-}R\text{-}y \longrightarrow \text{-}R\text{-}z\text{-}$

2,2 $x\text{-}R\text{-}x + y\text{-}R'\text{-}y \longrightarrow \text{-}z\text{-}R\text{-}z\text{-}R'\text{-}$

2,3 $Rx_2 + Ry_3 \longrightarrow$ more complex polymers

A number of synthetic resins and their polymers have been studied by Kienle (86) who found that the non-convertible, linear, 2,2 polymers had long chains of high molecular weight while the convertible polymers had short twining chains of only moderate molecular weight. He has listed a number of reactants and their probable functionality:

Reacting Substance	Functionality
Styrene	2
Formaldehyde	2
Cyclopentadiene	2
Phenol (acid catalyst)	2
Glycol	2
Phthalic anhydride	2
Oxygen	2
Phenol (basic catalyst)	4
Glycerol	3
Cyclopentadiene (heat and pressure)	4
Drying oil	6-8

To these can be added those studied by Bradley (94).

Reacting Substance	Functionality
Succinic acid	2
Adipic acid	2
Sebacic acid	2
*Linoleic acid	2
*Linolenic acid	2
*Eleostearic acid	2
Citric acid	3 or more
Tricarballylic acid	3
Adduct of eleostearic acid and maleic anhydride	3 or more
Maleic anhydride	4

*These are normally two, but can become greater under unusual conditions.

According to Kienle (86) there are three fundamental postulates which are the keynote to resin formation and resin properties. He has concluded that:

(1) Organic compounds of high molecular weight will form only when the interacting molecules are polyreactive. To illustrate, consider the following reactions:-

acetic acid + ROH → ester (1,1)
succinic acid + ROH → ester (2,1)
succinic acid + glycol → linear polymer (2,2),

which is soluble, heat non-convertible, low molecular weight, microcrystalline and homogeneous;

phthalic anhydride + glycerol → glyptal (2,3),

which is crosslinked, infusible, heat convertible, viscous and insoluble.

(2) The interlinking proceeds according to the chance contact of any two reactive points. This leads to heterogeneity, complexity and other colloidal properties. The number of reactive points is still appreciable when the reaction stops.

(3) The relative size and shape of the reacting molecules and the position of the reactive points largely determine the physical properties of the polymeride. For example, the water resistance of the polymer decreases as we react higher alcohols with phthalic anhydride because there are free hydroxyl groups which remain unesterified due to the blocking action of the rapid, early gelation.

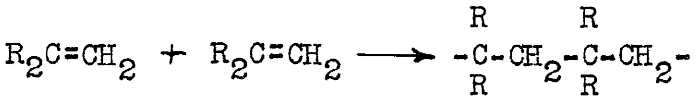
Also, a large distance between reactive points tends toward an open structure, softer and lower melting polymer.

IV. Mechanism Of Polymerization

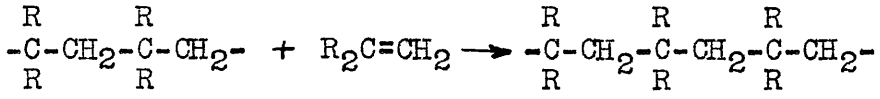
At least three different concepts have been utilized in an attempt to explain the manner in which the basic structural polymer units are built up. They will be discussed as chemical theories, colloidal theories and other theories which necessarily include certain concepts of the first two classes.

The chemical viewpoint, with which Standinger's (93) name is associated, is that the monomers are bound together by primary valences into large structural units. As the degree of polymerization becomes greater, the molecular weight increases and the length of the chain likewise increases. The chain is in effect a single molecule. When the chain length is relatively short, "hemi-colloids" are obtained. Longer chains lead to "eu colloids". The former have molecular weights from 2000-10,000 and single molecules containing 50-100 monomeric units. The latter have molecular weights from 10,000 to above 100,000 and chain lengths of as many as 3000 monomeric units. Eu colloids have higher viscosities, higher softening point and less stability at high temperatures.

Standinger (95) proposes the following mechanism involving free terminal bonds (free radicals):



$$R_2C{=}CH_2 + R_2C{=}CH_2 \longrightarrow -\underset{R}{\overset{R}{C}}-CH_2-\underset{R}{\overset{R}{C}}-CH_2-$$



$$-\underset{R}{\overset{R}{C}}-CH_2-\underset{R}{\overset{R}{C}}-CH_2- + R_2C{=}CH_2 \longrightarrow -\underset{R}{\overset{R}{C}}-CH_2-\underset{R}{\overset{R}{C}}-CH_2-\underset{R}{\overset{R}{C}}-CH_2-$$

The initial reaction must be activated by heat or other catalysts; the succeeding reactions are very rapid but decrease in speed as the chain lengthens. A similar theory has been proposed by Chalmers (96) who states that one monomeric unit must be activated after which a polymer chain builds up at almost an instantaneous rate. Carothers (97) indicates that free radicals or condensation reactions may be involved in the polymerization of substances like formaldehyde. Thus pure, dry formaldehyde might behave as follows:

$$CH_2{=}O + -CH_2-O- \longrightarrow -CH_2-O-CH_2-O-$$

In the presence of water, the following might occur:

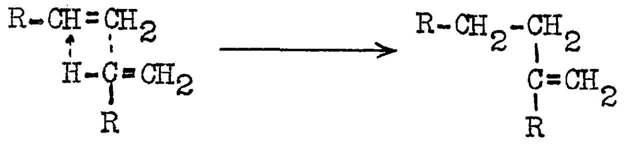
$$CH_2{=}O + HOH \longrightarrow HO-CH_2-OH$$

$$HO-CH_2-OH + CH_2O \longrightarrow HO-CH_2-O-CH_2-OH$$

In the presence of strong acid, water might be eliminated:

$$HOCH_2OH + HOCH_2OH + HOCH_2OH \longrightarrow HO-CH_2O-CH_2O-CH_2OH$$

Opposed to these free radical theories are those involving the migration of a hydrogen atom. The proposed mechanism might be this:



etc.

Stobbe and Färber (98) lend support to this hypothesis by the isolation of diindene of the structure

which may be formed by the wandering of a hydrogen atom. Whitmore (21) supports this theory but uses an ion concept:

$$(CH_3)_2\,C = CH_2 + H^+ \longrightarrow (CH_3)_3\text{-}C^+$$

$$(CH_3)_3\text{-}C^+ \quad + \quad (CH_3)_2C{=}CH_2 \longrightarrow (CH_3)_3C\text{-}CH_2\text{-}\underset{+}{C}\text{-}(CH_3)_2$$

Serious opposition to these stepwise theories of polymerization has come from Chalmers (96) who considers them inadequate to explain macropolymerization. If the rate of consecutive reactions is not greater than dimerization, then the dimer and other low polymers should be formed in largest proportion. Moreover, it should be possible to isolate the intermediate di-, tri- and tetramers. The absence of lower polymers at the beginning of and during the reaction has been noticed by Stobbe and Posnjak (99) in the conversion of styrene, by Stobbe and Lippold (100) in regard to ethyl itaconate, and by Lebedev and Mereshkowski (101) in the polymerization of diolefinic hydrocarbons.

However, these addition polymers are formed whether by labile H atoms or by activated free radicals, the end groups are left unsaturated and must either (1) be oxidized or otherwise converted to saturated groups, (2) solvated or (3) combined into rings. Carothers (85) does not consider that large rings are feasible. Since ring closure must be the last step the chains will be long and the chance of contact between reactive end positions will be slight.

The relationship between solubility and the length of chain is not easily discernible. No definite statements can be made. Polystyrene containing perhaps 1000 structural units is soluble whereas polycyclopentadiene containing 6 units is insoluble.

The relationship between convertibility and chain structure is well known. Reactants involving 2,2 functionality always yield linear non-convertible polymers. Reactants of higher functionality lead to cross-linked polymers which can be converted by heat to infusible resins. These concepts can be illustrated by considering the structures of various glyptal and Bakelite resins. These resins exist in three possible stages:

A stage: soluble in acetone; fusible $\xrightarrow{\text{heat}}$

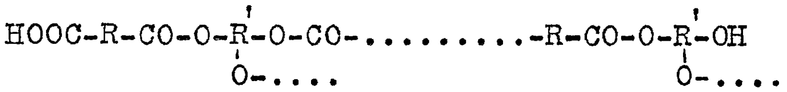
B stage: insoluble in acetone; difficult to fuse; not resistant to cold water; can be molded under pressure $\xrightarrow{\text{heat}}$

C stage: insoluble; infusible; resistant to water; can be molded under pressure.

The alkyd (glyptal) resins have the following structure:

HOOC-R-CO-O-R'-O-CO-..........-R-CO-O-R'-OH

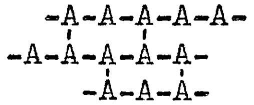
fusible, linear, non-convertible type



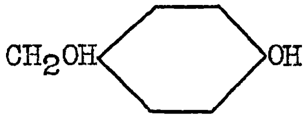
$$\underset{\text{O-....}}{HOOC\text{-}R\text{-}CO\text{-}O\text{-}R'}\text{-}O\text{-}CO\text{-}..........\text{-}\underset{\text{O-....}}{R\text{-}CO\text{-}O\text{-}R'}\text{-}OH$$

infusible, cross-linked, convertible type

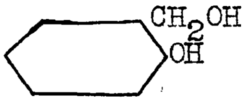
If "A" represents a monomeric unit containing a reactive group, the cross-linking action may result in



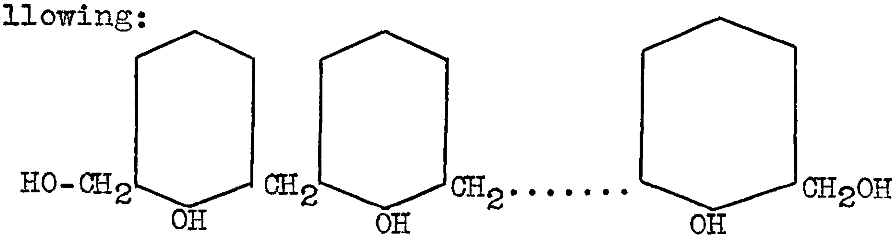
The Bakelite resins, phenol formaldehyde basic condensed polymers, form first two isomeric saligenins -



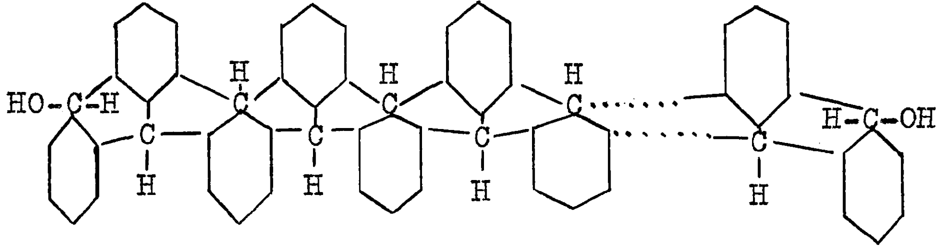
and



These continue to condense and polymerize rapidly to the A stage, which is represented by Blumfeldt (102) as the following:



The continued heating of this polymer transforms it quickly through the oil-soluble stage into large molecular aggregates of complex and indeterminable nature. This condensation might involve two molecules of Bakelite A to produce



or similar complex, cross-linked molecular aggregates.

The distance between reactive groups and the number of cross-linkages are important factors in determining the hardness, melting point and resistance to solvents. This may explain the better hardness of phthalate resins compared with citrate resins of the alkyd type. Jordan and Cutter (103) have found that ethylene glycol forms a hard, glassy resin with phthalic anhydride, whereas propylene glycol yields a softer, lower melting resin and diethylene glycol ($HOCH_2CH_2OCH_2CH_2OH$) yields a balsam-like resin. Similar results have been found for the condensation products of aminoarylsulphonamides and aldehydes, and for other resin combinations.

Opposed to the chemical theories are the <u>colloidal theories</u> such as those of Hess (104) and Pringsheim (105). They believe that the unit structures are monomeric or dimeric and are held together by secondary valence forces or by association (these Van der Waals forces are those which exist between electrically neutral molecules as a result of an interaction between the electrical and magnetic fields of the molecules).

X-rays have established definite periodicities in such substances as rubber, cellulose, polycyclopentadiene and polyoxymethylene. Originally this evidence was used to support the colloidal theory of polymerization. More recently, Mark and Meyer (106) have proposed a "micellar" theory where the high molecular weight organic compounds are considered to be linked together into chains by primary valence forces. Bundles of these chains are associated laterally by secondary valences to form micelles which act as units and lead to colloidal properties.

Other theories have been based on coordination and crystalline forces but these have not been generally accepted. Bergmann's (107) theory is that the structural unit is coordinated in the solid state and the unit, as such, is incapable of free existence in the vapor phase or in solution. Polysaccharides and proteins are thus built up of small units associated in the large molecules by supermolecular affinities similar to that of molecules in a crystal lattice. Long and McCarter (108) also compare forces of crystallization and the forces orienting monomer molecules into at least multiple units.

V. Factors Influencing Polymerization

Polymerization reactions are very sensitive to heat. Low temperatures are usually more suitable to the formation of long-chain polymers than high temperatures. Scheiber and Sändig (109) represent the effect as follows:

$$\text{Monomer} \quad \underset{\text{excessive temperature}}{\overset{\text{Suitable temperature}}{\rightleftarrows}} \quad \text{Polymer}$$

This may not always be true according to Carothers and Hill (110). The stability is probably a definite function of the nature of the polymer. Cyclopentadiene increases in polymer size on heating whereas polyoxymethylene liberates formaldehyde monomer when subjected to heat. Wornum (111) studied the glycerol-phthalic anhydride condensation and came to the conclusion that straight chain reaction occurs at low temperatures due to the inactivity of the β -hydroxyl group in glycerol. Gelation only occurs after long heating. At high temperatures 3-dimensional growth occurs immediately yielding a large number of small units. Cross linkages occur rapidly, bringing about phase complexity and gelation.

Catalysts such as stannic chloride, antimony pentachloride, acids, bases, salts and oxides in general act catayltically. Phenolic compounds such as quinol, resorcinol, guiacol and long sidechain phenols make effective inhibitors. For most unsaturated hydrocarbons, sulfuric or phosphoric acid is commonly used; the action is believed due to an ester which reacts and is subsequently regenerated.

Light and polymerization are closely linked. Light of long wave length aids the process whereas shorter waves favor dissociation. Certain types of molecules are more sensitive to activation by light than others, and the effect of light on polymerization reactions is undoubtedly of very great importance, particularly in the field of natural products.

Pressure is of especial use in effecting secondary condensations or rearrangements. Reduced pressure is likewise useful if volatile products are formed and are to be removed. Sometimes positive pressure must be used to enable the application of high temperatures to volatile reactants. Tammann and Pape (112) studied the effect of pressure on the polymerization of styrene, isoprene, vinyl acetate, dimethyl butylene and indene. They found that increasing pressure causes a decrease in the temperature at which polymerization occurs. Starkweather (113) obtained similar results using pressures of 2000-9000 atmospheres and temperatures between 20-74°C. His investigations were mostly concerned with substituted butadienes.

VI. Study of Polymer Properties

The resinous state is characterized in its formation by nuclei formation, supercooling and other crystalline and pseudocrystalline evidences. The polymerized product will exhibit viscosity, plasticity and other definite evidences of colloidal behavior.

One very convenient method for the following of the course of a resin reaction of the additive type is the change in refractive index. The disappearance of double bonds lowers the refractive index. Condensation reactions cannot be followed in this way because no unsaturation changes are involved. Condensation reactions of the phenol-formaldehyde type cause an increase in refractive index. In styrene and tung oil the refractive index decreases.

Katz (114) applied X-ray diffraction methods to the study of polymerization. Using styrene, indene, tung oil, isoprene, dimethylbutadiene and erythrene, he found that the diffraction ring was the same for the unpolymerized substance as for the polymer. On the other hand, ethyl cinnamate, methyl ethyl ketone and methyl acrylate showed marked changes. Sheppard (115) states that the degree of polymerization can be determined from the diminution in diameter of the innermost diffraction rings arising from multiplanar reflections.

Bingham and Spooner (116) have developed a method based on viscosity to measure the degree of association. They applied their method to twenty-three octyl alcohols and found that polar groups accentuate association. Hydrocarbon residues are little associated and tend to lower association. Stereochemistry is also a factor; the more exposed the polar group is, the greater is its effect.

The determination of molecular weight is a valuable aid in the study of polymerization reactions. Some of the methods used are:

(1) Ultracentrifuge in which the relationships between the concentration of solution at two different points from the center of rotation is measured. The equilibrium between sedimentation and diffusion is the determining factor.

(2) Density, refractive index, solubility, volatility, etc., compared with analogous compounds.

(3) End group estimation, if the basal units and end groups are known.

(4) Viscosity, correcting for ring and other effects.

POLYMERIZATION OF FATTY ACIDS

I. Chemical Theories

Bauer (118) heated α and β eleostearic acids in CO_2 at 200° C. and obtained a thick oil together with volatile acids, hydrocarbons and water. The acid number and iodine number were lowered but the saponification number was increased. He considers that anhydrides and estolides have formed together with non-volatile acids of lower molecular weight. The molecular weight of the α-acid product was 4588 in benzine and 2285 in camphor; that of the β-acid product was 986 in benzine and 490 in camphor. Upon hydrogenation, the α-product yielded stearic acid and a little β-eleostearic anhydride; the β-product yielded a thick oil but absorbed considerable hydrogen.

Chowdhury and his associates (119) studied several unsaturated fatty acids. They conclude that linoleic acid polymerizes through a double bond conjugated system rather than through a carboxyl group. In the polymerization the acid value remains constant, the iodine value falls and the viscosity increases. Ricinoleic acid polymerizes with no change in acid or iodine values. The drop in acetyl value indicates a condensation of hydroxyl groups. These acid polymers can be decarboxylated to highly viscous hydrocarbons similar to lubricating oils.

Their views are opposed by Hilditch (120) who studied the results of numerous investigators. He states that their results indicate that free fatty acids differ from esters in showing an apparent increase in molecular weight. This shows that the free carboxyl groups are taking part in molecular aggregation.

Bradley (121) has shown that the acids of linseed oil and tung oil do not readily gel on heating because they tend to form only linear polymers.

II. Colloidal Theories

Although certain facts, in particular hydrogenation results, cannot be explained by a pure chemical viewpoint, the colloidal association theory has never received much attention in this particular field. No mention of it has been found in the literature.

POLYMERIZATION OF SYNTHETIC ESTERS

I. Chemical Theories

Carothers and Arvin (122) prepared and studied a number of polyesters. They consider the structures of these polymers in the light of the functionality concept. Polymerization is the chemical aggregation through primary valence bonds yielding linear, non-convertible polymers if the functionality is 2, 2, and cross-linked, convertible polymers when the functionality is 2, 3 or higher.

Mazume and co-workers (123) heated ethyl eleostearate and methyl linolenate at 300° C. in an atmosphere of hydrogen. The former doubled in molecular weight but the iodine number did not decrease much. The latter showed a decrease in iodine value proportional to the increase in molecular weight. They consider the polymerization a strictly extramolecular phenomenon.

In their study of the polymerization of ethyl linolenate at 300° C. in CO_2, Steger and van Loon (124) found both highly and slightly dispersed constituents. They consider the latter as polymerizates. The former are probably isomers of the ester having a cyclic structure. Since these cannot be polymerized, the ester will never completely aggregate.

Waterman and Vlodrop (125) studied the transformation of esters of unsaturated acids with and without hydrogenation catalysts in the absence of hydrogen. They heated ethyl esters of eleostearic, linoleic and oleic acids at 180-200° with and without 5% Ni on guhr and 5% Pt on carbon. The oleate was unchanged; the eleostearate was slightly changed. The linolate became polymerized through a rearrangement to a conjugated system.

Kino (126) has indicated the presence of dimers in the polymerization products of ethyl linolate and linolenate. He heated the esters in H_2 at 300° for 2-10 hours. After removing the monomer by vacuum distillation and methyl alcohol extraction, he claims to have obtained dimeric products.

Bradley (121) prepared ethyl and glycol esters of the fatty acids of linseed and tung oils and measured their heat convertibility. Under his conditions these esters did not polymerize to solid gels. In an earlier paper, Fonrobert and Pallauf (127) found that free fatty acids or their ethyl and glycol esters were not heat convertible and always remained in a liquid, soluble condition.

Bradley, Kropa and Johnston (128) prepared maleic and succinic glycol polyesters and determined their heat convertibility, acid number, viscosity, refractive index and other properties. During the formation of these polyesters the carbon-carbon double bond of the acid radical becomes active and undergoes an addition polymerization which, when sufficiently extensive, results in conversion of the polyesters to insoluble and infusible form. The succinate esters were prepared as reference standards of a bibifunctional condensation reaction. Unless condensation has progressed sufficiently to provide an average molecule containing at least two C-C double bonds, it has not been found possible to effect conversion by means of addition polymerization alone. Their results are based on the justifiable assumptions that the number of units of condensation (one molecule of dibasic acid and one molecule of glycol) per average mol of polymer can be calculated from the acid number. From this can further be calculated the average molecular weight and average chain length. The glycol succinate may then be used as the condensation standard and enables the determination of the amount and extent of addition polymerization taking place in glycol maleate.

II. Colloidal Theories

As in the case of fatty acids, no work has been reported on the association of synthetic esters.

POLYMERIZATION OF SYNTHETIC GLYCERIDES

The synthesis of glycerides is still in the experimental stage. Long and his associates (129) have shown the many difficulties encountered. Further condensation with the elimination of water occurs either during or subsequent to esterification. Also the wandering of the acyl group in glycerides is ill-understood as evidenced by the work of Fairbourne (130) and Hibbert (131).

I. Chemical Theories

Beal (132) heat bodied synthetic glycerides, extracted with acetone and determined iodine and acid values of both fractions. Oleic di- and tri-glycerides do not gel and remain completely soluble. Oleic monoglyceride gels; this indicates that the condensation of water from two molecules is more important than the presence of double bonds. Double bonds are effective, however, as shown by the nongelation of stearic monoglyceride. Synthetic glycerides of the mixed acids gel faster than the oil itself.

Standinger (93) and others believe that glycerides polymerize through normal covalent linkages, similar to those involved in styrene and other polymers.

Bradley (121) agrees with Beal's theory of ether formation in the polymerization of mono- and di-glycerides. He cites the following evidence in support of this contention:

Material	Time to Gel After Reaching 280° C.	Loss in Weight
	(minutes)	(%)
Tung oil	10	0.05
Tung diglyceride	70	0.89
Tung monoglyceride	100	7.8
Linseed oil	220	3.3
Linseed diglyceride	280	6.1
Linseed monoglyceride	360	11.5

Another explanation of this loss in weight during gelation might be a decomposition of the mono- and di-glycerides with attendant elimination of excess glycerol and formation of the tri-glyceride. However, Bradley considers ether formation more probable. Fonrobert and Pallauf (127) detected similar gel formation and consider decomposition or rearrangement with probable formation of triglyceride as the modus operandi.

II. Colloidal Theories

Morrell and Marks (133) investigated the properties of β-eleostearic glyceride. They found definite evidences of molecular association. The ether-insoluble portion of the gel was methylated yielding a fraction insoluble in petroleum ether and another soluble in petroleum ether. The former is associated giving molecular weights varying from 2114 in benzene to 444 in a certain concentration of acetic acid. The other is normal giving molecular weights varying from 440 to 370 in different solvents. The non-associated solvents tend to associate the solute, whereas associated solvents tend to dissociate the solute and give lower molecular weights. They point out the effects of solvents on the accuracy of iodine value determinations.

Long, Egge and Wetteran (134) studied the action of heating and blowing on linseed and perilla oils and the glycerides derived from their crystalline hexabromides. Ultimate analysis indicated that linolenic monoglyceride was formed. At 293° C., this glyceride decomposes rapidly with the evolution of acrolein, CO_2 and water. At 225° C., thickening reactions are slight but the hexabromide number decreases rapidly. Since the iodine number only decreases 3.7 points, an isomer is probably formed. This synthetic monoglyceride solidifies when its molecular weight rises above 1700. Up to this gelation point, large quantities of water are evolved. Molecular weight changes indicate this water comes from elimination of OH in the early part of the run. They consider that gel formation builds up from tiny particles of gel (nuclei). These nuclei are associated molecules dispersed in the original oil. As the solid phase grows, a point is reached where the liquid becomes absorbed by the gel particles and setting occurs.

Long, Rheineck and Ball (135) in a later paper introduce a new concept. They state that bodying partially uses up the free energy of the double bonds through association or polymerization processes. A larger, more complex and more polar molecule is formed which has a strong tendency to associate with neighboring molecules to form a solid gel.

POLYMERIZATION OF DRYING OILS

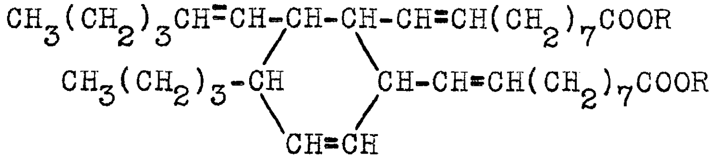
I. Chemical Theories

Krumbhaar (136) heated linseed and chinawood oil in CO_2 at 200°, 260° and 300° C. He determined acid value, iodine value, saponification number, viscosity, refractive index and specific gravity. Analogous changes were formed for both oils except in refractive index - this value increased for linseed oil. The speed of gelation of tung oil was faster than that of linseed oil, but he believes this effect is accentuated by the free acids liberated due to the longer time of heating for linseed oil. These free fatty acids tend to prevent gel formation; if they are removed by vacuum distillation, the oil suddenly stiffens. Gelation is a solubility phenomenon; the polymer is partially soluble in the unchanged oil up to saturation, at which point it is thrown out as a gel.

Milas (137) regards polymerization as a chain mechanism which requires light, oxygen or some other antocatalyzer. As evidence he cites the work of Stobbe and Posnjak (99) on styrene and of Monreau and Dufraisse (138) on acrolein. The latter found that light or oxygen is necessary to change acrolein to disacryl. Excess oxygen causes oxidation and polymerization.

Ellis (82) states that tung oil polymerizes by a

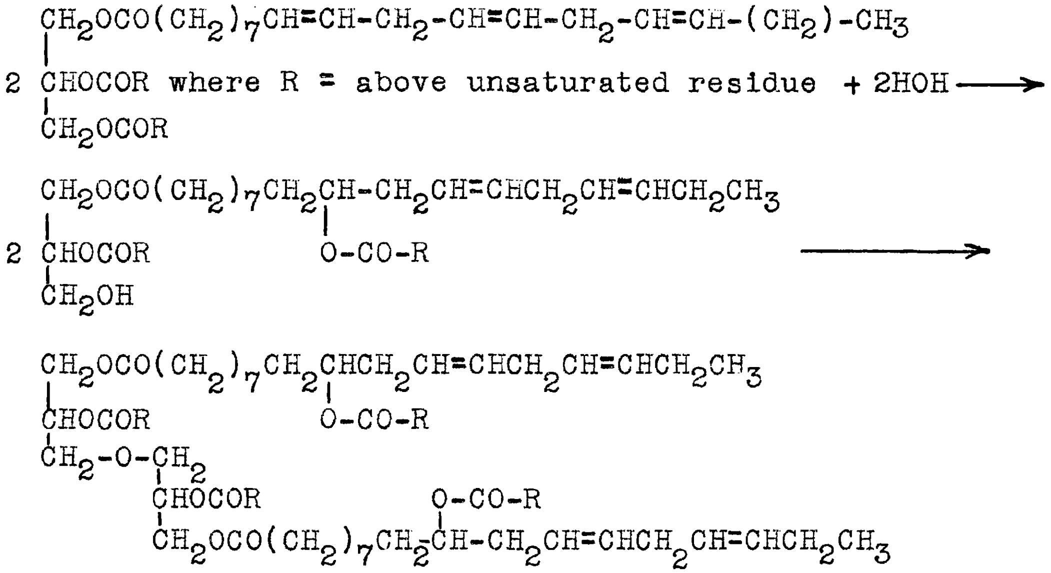
Diels-Alder mechanism which may be intra or intermolecular. Eleostearic acid can condense with itself to produce a structure.



In this aggregation, α-eleostearic adds away from the carboxyl group. The α-product is difficult to dry and does not resist benzene. The β-product dries readily and then will resist benzene. Tung oil is also known to polymerize at 50° C. if subjected to a pressure of 500-600 atmospheres. The refractive index decreases and in three hours, a viscous product is formed. Longer treatment produces a waxy gel.

Kappelmeier (139) in a recent article also considers the thermal polymerization of tung oil and oiticica oil as a Diels-Alder reaction leading to cyclohexenes. Linseed oil and perilla oil isomerize to a conjugated system and then polymerize to cyclohexene derivatives. In their cases, however, a longer time and a higher temperature are required; free acid is also formed.

Salway (140) proposes a theory of oil boiling which premises the liberation of free fatty acids, which condense at the unsaturated linkage of the oil. This liberates a glyceryl OH group, which condenses with similar free hydroxyl groups to form polyglyceryl derivatives. Schematically, he represents his mechanism as follows:



$$2\ \begin{array}{l} CH_2OCO(CH_2)_7CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2){-}CH_3 \\ | \\ CHOCOR \text{ where R = above unsaturated residue} \\ | \\ CH_2OCOR \end{array} + 2HOH \longrightarrow$$

$$2\ \begin{array}{l} CH_2OCO(CH_2)_7CH_2\underset{\displaystyle |\atop \displaystyle O{-}CO{-}R}{CH}{-}CH_2CH{=}CHCH_2CH{=}CHCH_2CH_3 \\ | \\ CHOCOR \\ | \\ CH_2OH \end{array} \longrightarrow$$

$$\begin{array}{l} CH_2OCO(CH_2)_7CH_2\underset{\displaystyle |\atop \displaystyle O{-}CO{-}R}{CH}CH_2CH{=}CHCH_2CH{=}CHCH_2CH_3 \\ | \\ CHOCOR \\ | \\ CH_2{-}O{-}CH_2 \\ \qquad\quad | \\ \qquad\quad CHOCOR \\ \qquad\quad | \\ \qquad\quad CH_2OCO(CH_2)_7CH_2\overset{\displaystyle O{-}CO{-}R \atop \displaystyle |}{CH}{-}CH_2CH{=}CHCH_2CH{=}CHCH_2CH_3 \end{array}$$

To support his theory, he states that the iodine value decreases proportionately with the decrease in acid value. Further, unsaturated acids are known to add H_2SO_4 easily. Fahrion (141) considers that a similar reaction can take place in two unsaturated acid molecules. Free fatty acid accelerates the rate of bodying, whereas free glycerol hinders the action. As far as the second reaction is concerned, it is well known that glycerides lose water at high temperatures. Monoacetin is readily changed to diacetyldiglycide. Long (129) observed the production of abnormal amounts of water in the synthesis of various glycerides. Further support of this theory is found in the work of Kitt (142) and Long (143). Kitt observed an apparent loss of glycerol during heat bodying. He believed that free fatty acids were produced and subsequently condensed to lactones.

Long and Wentz (143) studied the rate of molecular weight increase in the boiling of linseed oil. The decomposition, which occurs at 293° C. and over, was originally thought to be an aldehyde condensation. This idea was rejected because (1) no tests for aldehydes could be found, and (2) the introduction of acrolein in the nitrogen stream did not appreciably alter the rate of bodying. However, the addition of 10 per cent free fatty acid produced a great increase in rate. The molecular weight determinations indicate that a chemical condensation has occurred. Without polyglyceryl condensation, the molecular weight increase would depend on the rate of formation of free fatty acid, which is rather slow. Since the experimental rate is rapid, this would support Salway's ideas.

Although Salway's theory explains the slight difference in saponification value, the decrease in iodine value, and the apparent reversal of polymerization by hydrolysis and conversion into simple esters,there are two objections, which have been raised: (1) hydrolysis occurs easier at the β -glycerol position than at the α -position (cf. Long - 144), and (2) hydrolysis should yield a condensed ether, tetrahydroxy, ethyl ether; this compound could not be isolated (cf. Cutter - 145).

Mazume and his assistants (123) polymerized tung oil and herring oil. They consider that extramolecular addition occurs as evidenced by an increase in molecular weight, which is more rapid than the simultaneous decrease in iodine value.

Waterman and Vlodrop (125) studied the change in specific refraction, $(n^2-1)/(n^2+2) \times 1/d$, compared to the change in unsaturation. A theoretical line for polymerization can be deduced if we assume that all the double bonds are saturated and the nature of the oxygen linkages are unchanged. This theoretical line is only reached near the end of the reaction. The high specific refractivity at the start is thought due to the formation of a conjugated system by isomerization.

In a previous paper Waterman and Oosterhof (147) vacuum distilled linseed oil and stand oil under conditions that the oil was in contact with the heated surface only 3-4 seconds. Linseed oil distilled unchanged but stand oil left a residue which dried better than the original oil, was clear, had a lower acid number and a higher molecular weight and viscosity. The distillate fraction had about the same iodine number and ultimate analysis, but it was cloudy and dried poorly. According to Meinel (148) the double bond in linolic and linolenic acids shifts to a conjugated system during the conversion of linseed oil to stand oil. He bases his qualitative results on the silver thiocyanate test.

Kaufmann, Baltes and Büter (149) studied the changes in iodine number, diene number and thiocyanogen number during the heat polymerization of drying oils. Oiticica and tung oil give initial rapid drops in diene number, but at gelation, this diene number is still quite high. The thiocyanogen number is not appreciably affected; the iodine number drops slightly. Linseed oil shows a drop in iodine number and thiocyanogen number; the initial small diene number decreases to zero.

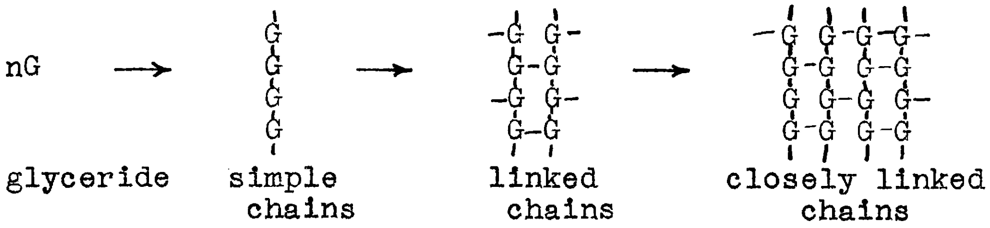
Morrell (150) in an early paper proposed the idea of isomerization as a preliminary requirement in the thermal polymerization of linseed oil and other non-conjugated oils.

With regard to the effect of oxygen in polymerization, Dostal and Marks (146) state that its presence lengthens chain duration, but hinders isomerization. The induction period may entirely disappear in the absence of oxygen.

Hilditch (120) considers the primary stage as intramolecular polymerization. The initial rapid fall in iodine value with only a slight increase in viscosity and density is due to a rearrangement of the valences between the unsaturated groups present either in a single fatty acid chain or between those present on the same glyceride molecule. The later changes are due to intermolecular polymerization between glycerides.

Gee and Rideal (151) in a recent article described their phase-boundary-potential studies on the catalyzed polymerization of monolayers of drying oils. A complex is formed with the catalyst, and this leads to addition polymerization in which the chain length rarely exceeds 10 units and usually is less than 5 units.

From the study of tung oil polymerization, Rhodes and Welz (152) conclude that the primary condensation is between two acid residues through primary valences to a cyclobutane ring, a finding which is opposed by Ellis (82), Kappelmeier (139), Jordan (153), and Brown (154). The latter examined the structures of many natural products and states that the abundance of 5 and 6 carbon rings in nature indicates similar formations in the oxidation and polymerization. Jordan argues that the 4 carbon ring is notoriously unstable, and although the 8 carbon ring would be the next most likely, circumstantial evidence favors the 6 carbon ring. He further states that glycerol takes no part in the condensations since it can be quantitatively recovered from polymerized tung oil by means of a hydrolysis which does not affect the acid residues. Whatever the primary change, whether to a 4, 6 or 8 carbon ring, eventually chains form with simple glycerides as links. At low temperatures these chains are side by side as single longitudinal chains; at high temperatures linkings between parallel chains develop through the primary valences. These mechanisms might be represented as follows, where G is the simple glyceride, trieleostearin:



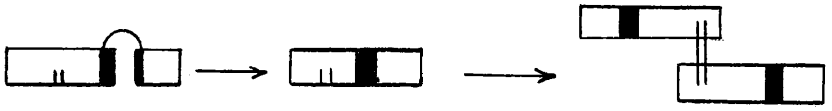
The changes which occur depend on time, temperature, free acid existing or formed, rosin or oil additions, sulfur additions, etc. Above 260° C. decomposition reactions take place and an insoluble gel is formed. Below that temperature a longer time is required to produce a gel, which never becomes completely insoluble. Free acid is said to increase the time of gelation; 10-15 per cent has an appreciable effect. This may be due to a radical interchange or to depolymerization. Rosin and other oils delay gelation due to their intercombination and dilution. The best film is produced if very large and complex molecules are judiciously combined with less complex ones to insure proper film formation. Temperature controls this ratio because the various components of tung oil polymerize with different velocities and have different temperature coefficients.

In a later paper, Jordan and Cutter (155) consider that the ring formation in the polymerization of tung oil involves 6 carbon atoms in all cases. Linseed oil polymerizes in a similar manner after a preliminary isomerization.

Bradley (156,94) has adapted the concepts of Carothers (84,85,97) and Kienle (86) to the polymerization and drying of fatty oils. As discussed in the section on polymerization, these concepts consider polymerization as ordinary reactions of organic chemistry proceeding in multiple fashion because of the multiplicity of reactive or functional groups present in the original polymerizing substance. Furthermore, condensation and addition reactions may be considered as similar phenomena. Using their functionality concepts, the conversion of an oil to a gel by means of heat is essentially the conversion of a linear structure to a cross-linked or three-dimensional form. The potential convertibility of the oil is therefore the determining factor for its ultimate gel formation. Convertible systems as we know must have a functionality greater than two. Although the term "functional group" has been applied to all groups which react in a polymerization - carbon-to-carbon double bond, hydroxyl and carboxyl groups, etc. - the mere presence of these groups does not ensure polymerization. The number of points on the unit molecule at which attachment to other groups becomes possible and the application of enough energy to activate these centers are also important factors. If intramolecular or bimolecular ring formation occurs, the plurality of functional groups may be decreased below the point where a three-dimensional structure can eventually form. A plurality of linkages between two molecules is no more effective in a polymerization reaction than a single connecting link. Obviously, both the number and type of reactive centers are necessary before unrestricted growth in all directions is a possibility. The natural drying oils are convertible hybrid polymers in the sense that both addition and condensation reactions are involved since their conversion to esters is but a step towards their complete polymerization. The only remaining functionalities are the double bonds. If a double bond is in a terminal position in an essentially hydrocarbon chain, polymers of unusually high molecular weight are easily formed; the functionality is considered to be two. Multiple unsaturation of the aromatic type is observed to be non-functional. Unsaturation confined within an aliphatic hydrocarbon chain is in a special category, which includes the natural drying oils. Molecular weight determinations of the soluble, polymerized forms of the drying oils and of their related esters have in all cases been of a comparatively low order, rarely exceeding that of a dimer.

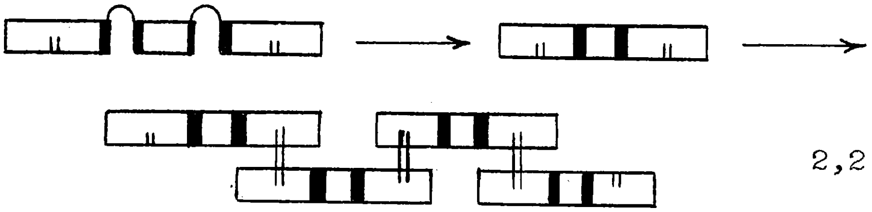
Dimerization through a bimolecular reaction involving ring formation is a characteristic property of both the conjugated and the nonconjugated drying oil acids and esters. This concept limits the functionality of the double bond system to one. The fatty acids therefore usually only have a functionality of two; they will combine with a trifunctional alcohol to yield a convertible polymer. The following diagrams indicate the structures which will arise when alcohols of one, two and three functional groups are reacted with a drying oil acid:

(1)



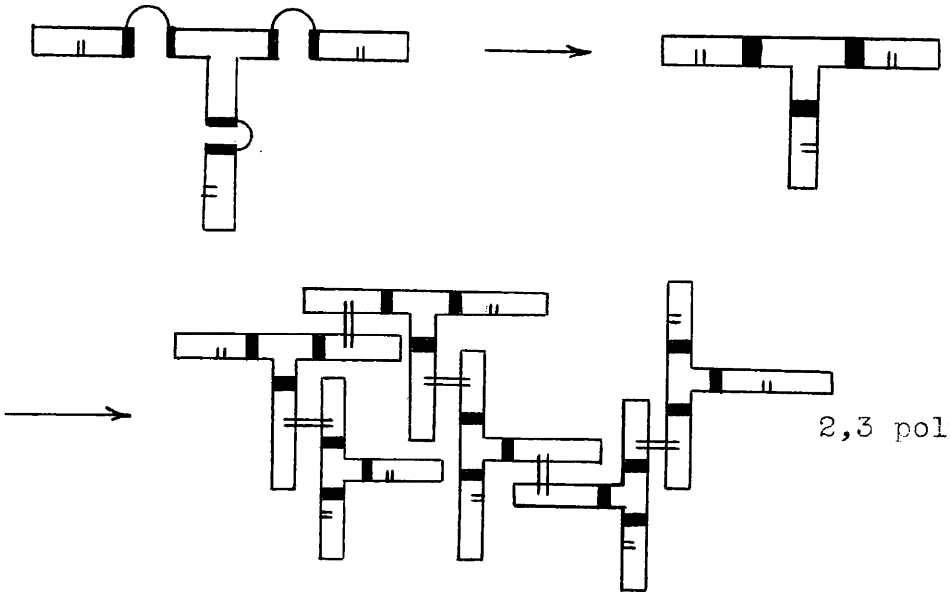
2,1 dimer

(2)



2,2 polymer

(3)



2,3 polymer

Saponification and hydrolysis will yield the dimers in all cases. As experimentally substantiated, the preliminary heat treatment will extend the degree of polymerization and require less energy to effect the ultimate conversion. Likewise, anything which prevents an active group from functioning will restrict the polymerization and inhibit or prevent the ultimate conversion. Thus an excess of glycerol which can effect the condensation mechanism through mono- or diglyceride formation will inhibit the ultimate conversion. These functionality concepts have now been adopted by Kienle (157) and by Houwink (158).

Popkov (159) has given a comprehensive review of Staudinger's theory on the three dimensional molecular structure of highly polymerized substances. In another recent article, Cutter (160) has summarized the evidence and theories relating to the polymerization of drying oils. He states that the heat bodying of oils exposed to the atmosphere results in decomposition above a certain temperature with the elimination of water and low molecular weight acids and aldehydes. This definite but not extensive reaction precedes bodying and continues throughout the process. During polymerization there is a decrease in iodine and hexabromide values, and an increase in refractive index and viscosity. The first two values fall rapidly in the beginning, a phenomenon which has been associated with the disappearance of some linolenic acid derivatives. Any real viscosity increase occurs after this change during which the acid number rises. Tung oil bodies with different property changes; no decomposition occurs, the refractive index falls, and the acid value either remains constant or falls slightly. Along with Kronstein (161), Fahrion (162), and others, he suggests a true polymerization of two molecules to form a ring complex.

II. Colloidal Theories

Kitt (163) was one of the first investigators to suggest that bodying occurred through the colloidal association of two molecules of glycerides. Several years later Norman (164) proposed the same idea.

Wolff (165), in a series of papers, points out that the important property of a bodied oil is its viscosity, which is unrelated to the iodine value. Further, molecular weight determinations vary according to the solvent; this indicates that extramolecular association predominates over real polymerization. He states that a two phase isocolloid is formed, but does not explain how the second phase arises.

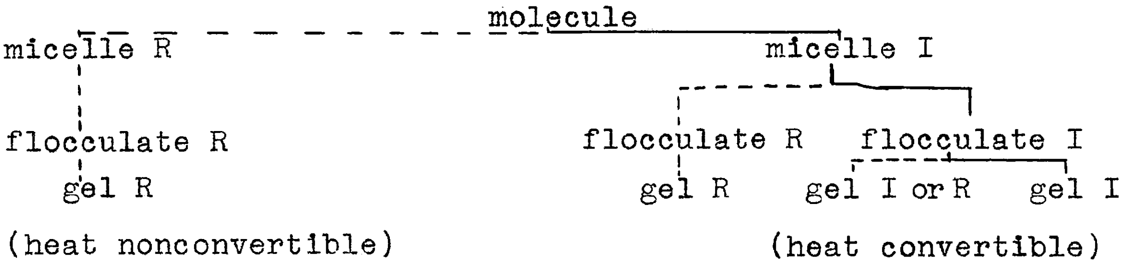
A similar viewpoint has been expressed by Auer (166). His original papers appear in various German and American journals from 1926 up to the present, but a summary of all his work is found in the indicated reference. He considers that fatty oils are isocolloids which form solid films in thin layers as a result of the action of gases. These gases behave as electrolytes in coagulating lyophobic colloids; a certain threshold concentration must be reached. The gases are adsorbed by the film, but this adsorption is a secondary process and is not essential to film formation. Gas coagulation occurs at the gas-liquid interface, and it is influenced by capillary active compounds. Etheric oils retard film formation, and metallic soaps accelerate it. Formic acid separates the phases of the isocolloid and the dispersed phase can form gels with non-fatty dispersion mediums like cylinder oils. Heat bodying increases the concentration of dispersed phase, probably due to small amounts of absorbed gases, such as oxygen. The oxygen is slowly driven off, and in rising to the surface creates an electrical condition which coagulates more dispersed phase. This is substantiated by the experimental observation that petroleum-ether-insoluble acids, considered to be oxyacids, are formed when oils are heatbodied in vacuum as well as when they are blown in oxygen. However, the acids formed in heat bodying contain less oxygen than the original acids, showing that their formation is not connected with chemical oxidation.

Dorn and Erastova (167) isolated two phases from linseed oil. The constants of the system produced on mixing these phases are the same as those of a heat polymerized oil. They conclude the latter must be a colloidal dispersion system.

The associated structure of heat bodied oils is supported by Morrell and Marks (168), who explain the variations of molecular weight and iodine number with the nature of the solvent on that basis.

Wornum (169) has classified the disperse phase systems in the following manner:

____ = primary valence linkage ----= secondary valence
I= irreversible R = reversible



Two aspects are present: (1) the manner of micelle formation, and (2) the spatial distribution of units and its relationship to phase stability (a factor in the sol-gel transformation). A 2,2 flocculate can only result through secondary valences. At high temperatures these colloidal complexes are evanescent and no gel is formed; when cooled, a reversible gel state is formed. The 2,3 and higher functionality forms may have the usual secondary valency influences at low temperature, but in addition, primary valences can take part at high temperatures with the formation of an irreversible gel. The first stage involves the formation of a complex molecule whose nature is modified according to the conditions, induced cross-linking and the directional activity of the units concerned. A new phase is formed; nuclei form and grow. The rate of nuclear formation increases faster with temperature than the rate of nuclear growth. High temperatures or other catalytic conditions will produce many nuclei and short chains. In the second stage, micelles are formed. These may be closely packed, but they are not necessarily oriented. The reactivity is concentrated at the surface and the same rate considerations apply as before. In the third stage, flocculates are formed. These reactions depend on the activity of simple molecules, which accounts for the faster gelation of tung oil. Below 270° C., the acid in the β -glyceride position is insufficiently energized to crosslink. At 270° C. the rate is relatively slow, and large size flocculates form. Around 310° C. smaller units form, and more of the original oil is changed before gelation occurs. Higher temperatures tend to yield decomposition products which are adsorbed on the micelle surfaces and tend to destroy flocculate growth. If the spatial distribution is uncontrolled, true micellar dispersion soon changes to flocculates whose stability depends on their shape and size. The gel change is essentially only a change in spatial distribution. Oil properties are determined by: (1) micell aggregates cannot pack as closely as micelles, and thus retain some reactivity such as liquid adsorption (swelling), and (2) dispersing agents may be added to stabilize the true micelles and thus control the ultimate particle size. These agents probably orient at the active points and reduce the possibilities of further crosslinking; they must be polar compounds. Fatty acids are ready dispersing agents for this purpose.

Long (170) expressed the view in 1929 that the molecules polymerize by orientation in which secondary valence forces at the double bonds are the binding forces. No primary action and no four or six carbon rings are formed. Zimmerman (171) showed that the semisolid bodies produced in heat bodying are gels. In a later article Long, Rheineck and Ball (135) speak of the free energy of the double bonds. They regard heat bodying as a process which partially uses up this free energy by association of molecules to form a more complicated and polar molecule which has a strong tendency to associate with neighboring molecules to form a solid gel. A similar view is expressed by Long and McCarter (108). They view the increase in acid value on heating as a cleavage at the fifteen and twelve double bonds, and cite the presence of low molecular weight acids and aldehydes in the vapors as evidence for their statements.

Long, Kittelberger, Scott and Egge (129) studied the orientation of heat bodied oils, using the methods of Langmuir. They found two distinct segments in their compression curves: (1) a point where pressure is first exerted and A_o, the area at zero compression (x -intercept), and (2) a break in the curve. The area at the initial pressure is a measure of the size of the molecule. In the early stages the decrease in area is greater than a straight line function of the force; this is due to more effective intermolecular attractions, and indicates that the attraction of molecules containing double bonds and other polar groups is a composite effect. At a certain force the molecules touch and increasing forces cause crumpling of the film. Their measurements indicate definite orientation dependent on the presence or absence of polar groups. The external crumpling force becomes less as the number of double bonds increase. This supports the theory that the double bond forces are tying the molecules together and thus aiding the external force in its work. This action in heat bodying would lead to polymerization.

Hilditch (120) regards the disposition of molecules at the interfaces between different parts of a heterogeneous system as an important factor in the study of aggregation. Blom (172) suggests that the wrinkling of tung oil films may be due to strains set up by the orientation of the least soluble molecules in the surface layers. However, Eibner (173) believes that this trouble is due to crystalline eleostearin or to its crystalline oxidation products.

Cutter (160) presents a critical discussion of polymerization theories in the light of certain experimental evidences. The hydrogenation of bodied oils should yield stearic acid glycerides if the molecules are colloidally associated; if chemical ring formation is involved, the hydrogen may react but only complex products will result. Bauer (174) treated α-and β-eleostearic acid at 200° C. in a CO_2 atmosphere. Hydrogenation of the α-polymerized acid gave a large yield of stearic acid; that of the β-polymerized acid gave a syrupy, complex mixture. Gieth (175) hydrogenated bodied linseed oil and obtained a good yield of stearic glyceride. However, he found a second portion of oil which resisted hydrogenation.

The viscosity of a colloidal solution is a function of conditions. Since the volume of liquid through a capillary varies more rapidly than the pressure, the viscosity coefficient must vary with the shear. Slansky (176) and Ostwald (177) examined many oils by means of an apparatus of low shear rate. The viscosity variation with shear was especially pronounced with bodied oils; they conclude that heat-treated oils have two phases.

The dispersion of bodied oils in solvents is an indication of colloidal nature. Associated liquids such as water are excellent ionizing (dissociating) solvents. Non-associated liquids such as heptane are indifferent, non-ionizing (associating) solvents. In general, hydroxyl groups are important factors for imparting a high degree of association to an organic solvent. Molecular weight determinations have been made on various oils, using different solvents. Friend and Alcock (178) showed that the molecular weight in benzene varies with the concentration of the oil. Seaton and Sawyer (179) found variations using chloroform and benzene, but obtained constant values using stearic acid as the solvent. The unreliability of molecular weight determinations has been shown by Norman (180), Morrell (181), Long (182), and others. The explanation for this might be that benzene and chloroform are normal liquids and allow association of the oil to varying degrees, dependent on the oil concentration. On the other hand, stearic acid is associated and hence will dissociate the oil to the maximum extent; the molecular weight will be independent of oil concentration. Iodine value determinations and liquid extraction experiments have shown similar results. Morrell (183) found that paraffin solvents extracted much less unpolymerized oil than did carbon tetrachloride, an associated solvent. Auer's formic acid extraction is probably a similar phenomenon.

X-ray diffraction patterns are usually simple, broad diffuse bands which are believed to represent the nearest approach of molecules or aggregates. The degree of association can be calculated, and its value agrees with other data. Katz (184) examined tung oil but could find little or no change before and after heating. Clark (185) found that polymerization introduced a new ring of smaller diameter (i. e., larger spacing). This indicates the presence of associated aggregates.

From these evidences, Cutter concludes that bodied oils are associated liquids. The primary change occurs in the glycerides before the association change produces the bodied oil. This primary change determines the degree and type of association. The longer bodying time of linseed oil is believed due to the inactivity of the oleic and linoleic glycerides. Cis-trans isomerism in the oil may be an important factor.

Reviews of polymerization theories and methods may be found in various periodicals (186-195). No attempt has been made to pass on the excellence of these dissertations.

OXIDATION

Oxidation of oils and related products usually refers to oxidation by means of gaseous oxygen in some form. Air is the cheapest, available oxidizing agent, but at the same time it is the most difficult to control. To induce molecular oxygen to react at commercially useful rates, it is usually necessary to provide a catalyst and/or elevate the temperature. In the case of oils, only liquid phase processes are involved. Provision must be made to secure intimate contact of oxygen and oil-catalyst mixture, to initially raise the temperature, and to later remove reaction heat. Natural processes of heat flow may suffice if the rate of reaction is slow and low temperatures are being used. A number of commercial applications have been successful; for example, the oxidation of acetaldehyde to acetic acid, ethanol to acetic acid, hydrocarbons to acids, indigo synthesis, etc.

The oxidation of hydrocarbons is of especial interest because of possible analogies with the oxidation of drying oils. The usual method has been to inject air or oxygen into the heated oil and allow it to bubble through a relatively thick layer of oil. Catalysts have been necessary to lower the reaction temperature. Difficulties are numerous; acids tend to be aldehydic and hydroxylated in character; undesirable esters and other oxygenated compounds are formed; gums tend to be deposited; polymerization and condensation reactions which occur during the subsequent saponification operations give undesirable colors and odors to the product; separation of unoxidized hydrocarbons from the products is often difficult, etc. Volatile compounds, other than carbon oxides and steam, also form, and may be recovered from the gases leaving the oxidation zone. Small quantities of the lower fatty acids, such as formic, acetic, propionic, etc., are produced and may be recovered with the water-soluble volatile products by scrubbing the exit gases with water, or by extracting the oxidation mass with water.

In general soluble catalysts have been used in the form of fatty acid salts, alcoholates, etc., of the metals capable of existing in combination in more than one valence form. Manganese compounds, such as the acetate or stearate, form good examples of the catalyst types. Cobalt and mercury catalysts tend to increase gum formation, and lead catalysts are of low activity. Catalyst mixtures consisting of at least one compound of an alkali metal and of aluminum have been found effective. With one per cent manganese stearate in a paraffin wax, it is possible to oxidize at a temperature of 125°C. by injecting air, so that after eighteen hours a product with a saponification number of 232 and an acid number of 108 is obtained. As much as 15 to 20 per cent unsaponifiable matter remains in the product, even after prolonged injection of oxygen. Without catalysts, oxidation does not start at a useful rate until a temperature of 150 to 160°C. is reached and does not become rapid until somewhat higher temperatures have been attained.

Even with a catalyst, long periods of time are necessary for the oxidation of a batch of oil or wax to approach completion when air is simply bubbled through the liquid. By bringing about very intimate contact between air and the hydrocarbon oil to be oxidized through the formation of a foam of the liquid, the time of oxidation and the temperature for oxidation are both considerably reduced, losses through formation of low-molecular-weight oxidation products decreased, and the yield and quality of product increased. One method proposed for accomplishing this end is to admit air through a porous diaphragm in order to induce a frothy condition in the material being oxidized, and to recirculate a portion of the reacting material through an external heat exchanger for temperature control. By continuously admitting unoxidized material and withdrawing oxidized product in regulated streams, the process may be made continuous. Either dissolved catalysts or solid catalysts fixed in place with fluid passing over them may be used. Oxidation of crude paraffin wax (m.p., 50°C.) with air in the presence of a dissolved manganese catalyst for eight hours at 110 to 115°C. in such an apparatus yields a yellow product having an acid number of 95 and a saponification number of 152. Light-colored fatty acids having a saponification number of 220 may be recovered. Since the rate of reaction increases with increase in oxygen concentration, the use of enriched air, oxygen, or air under pressures of from 150 to 500 lb. per square inch has been advocated. To reduce the troublesome polymerization and condensation reactions attending the oxidation, the liquid hydrocarbon may be diluted with oxidation resisting substances such as acetic anhydride or other low-molecular-weight organic acids or anhydrides.

The composition of the product is generally so complex as to defy chemical analysis for identification of the constituent compounds. It is consequently difficult to postulate any definite series of reactions for the oxidation. Based on the experience of the I. G. Farbenindustrie A-G., Krauch (196) has, however, proposed a tentative scheme for the oxidation mechanism by postulating that oxygen attacks the paraffin molecule toward the middle and not on the ends. This proposal is supported by the facts that a portion of the acids formed contains about half the number of carbon atoms as the original paraffin molecule and that the small amounts of carbon oxides and low-molecular-weight oxidation products preclude oxidation from one end of the large molecules to form the acids in the product.

The formation of an acid product having an average chain length of 12 to 14 carbon atoms, as calculated from the equivalent weight of the acid product, from a paraffin wax averaging 24 carbon atoms per molecule, would seem to substantiate this postulated mechanism (197). However, the fact that such an acid product consists of a variety of acids of varying chain length makes it seem more probable that the oxygen attack is distributed and that rupture may occur at various points in the affected molecules. This action of oxygen on the high-molecular-weight paraffinic hydrocarbons at moderate temperatures and in the liquid phase is contrary to that noted in the vapor-phase oxidation of the lower-molecular-weight hydrocarbons at more elevated temperatures, where oxidation starts at the end of the longest carbon chain present in the molecule and continues from this point. The small amount of gaseous products obtained in the liquid-phase process precludes the possibility that the lower-molecular-weight products are produced by the progressive destructive oxidation of the high-molecular-weight starting material, and the low temperatures seem to eliminate the possibility that thermal decomposition can account for the low-molecular-weight material obtained.

OXIDATION OF FATTY ACIDS

In these discussions on the oxidations of acids, esters, oils, etc., frequent reference will be made to theories which were discussed in detail in the section on polymerization. Furthermore, only oxidation by air or gaseous oxygen will be considered. The action of oxidizing agents on the pure acids of the drying oils can be found in any standard organic textbook, such as Whitmore (21).

I. Autoxidation

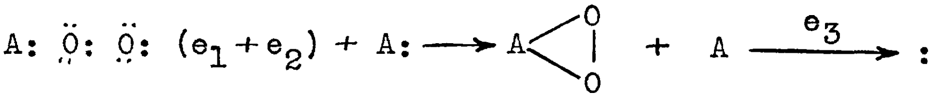
Milas (199) has presented an excellent review on autoxidation and includes 274 references on this subject. The criteria of autoxidation reactions are as follows: (1) They are autocatalytic; (2) They are susceptible to catalysts; (3) They can induce the oxidation of otherwise unaffected substances; (4) They can induce the polymerization of autoxidants; (5) They are sometimes chemiluminescent; and (6) Susceptibility and structure of the autoxidant are related. Several methods are available to study an oxidation reaction: (1) Quantitatively measure the oxygen absorbed in a unit time, and (2) Quantitatively measure the disappearance of the autoxidant or the progressive formation of the principal products in a unit time. The first method involves measuring the change in volume at constant pressure, or the change in pressure at constant volume. This requires equilibrium conditions, an improbability with linseed oil because of surface films which diminish the diffusion rate of oxygen. Morrell (200) states that skinning and agitation overcomes these difficulties. However, changing pressure will influence the rate of oxygen absorption; also gaseous products will produce an apparent decrease in rate. The second field of study has shown several possibilities. If there are no volatile products, the weight increase of the autoxidant may be measured. The oxidation of lubricating oils, which are non-acidic, may be followed by measuring the organic acids produced. Density, refractive index, viscosity and iodine number have all been used to follow the oxidation of drying oils (cf. Wagner and Bier - 201). If stable peroxides are formed, these may be quantitatively titrated. Trillat (202) has used the methods of X-ray spectroscopy. He spread thin films of the fatty acids on lead plates and took spectra immediately, at 2-3 hours, and at 40 hours. The first corresponds to that of the lead salt, the second to moloxide formation and double bond saturation, and the third, which has no spectra, to complete polymerization. His results show that the addition of oxygen to a double bond causes an elongation of the molecule equal to 6.78Å.

According to the old Engler - Bach theory, molecular oxygen adds to the double bond to form highly reactive peroxides. Baeyer and Villiger (203) offer much evidence in support of this. Opposed to this theory are several facts: (1) Peroxides have not been isolated; (2) Loss of hydrogen produces water or hydrogen peroxide, and (3) Other oxidizing agents work without the presence of oxygen. Weiland classifies the latter as dehydrogenation reactions, but cases have arisen where his theory also breaks down. Milas (204) proposes an electronic theory which apparently explains all the facts. According to his theory, the oxygen adds first to atoms or groups of atoms containing molecular valence electrons. This produces highly metastable or dative (semi-polar) bond peroxides. These peroxides may transfer energy to other molecules and produce new reaction chains by reverting to ordinary peroxides or by intermolecular rearrangement and subsequent splitting off of hydrogen peroxide or other organic peroxides. This theory assumes that (1) The autoxidants possess unshared or exposed electrons having their spins unpaired, (2) Molecular valence electrons are analogous to atomic valence electrons and (3) These electrons undergo a change in energy content (collision, radiation, temperature effects) and affect the entire molecule. The following scheme represents the probable reactions:

A: is a molecule of autoxidant
e_1 is the energy of activation
e_2 is the energy due to pairing of the spins of dative electrons.

$$A{:} + e_1 = A \xrightarrow{e_1} :$$

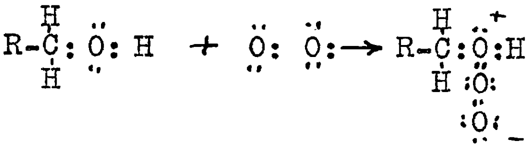
$$A \xrightarrow{e_1} : \ \ddot{\underset{\cdot\cdot}{O}}{:}\ddot{\underset{\cdot\cdot}{O}}{:} = A{:}\ \ddot{\underset{\cdot\cdot}{O}}{:}\ \ddot{\underset{\cdot\cdot}{O}}{:} \quad (e_1 + e_2)$$

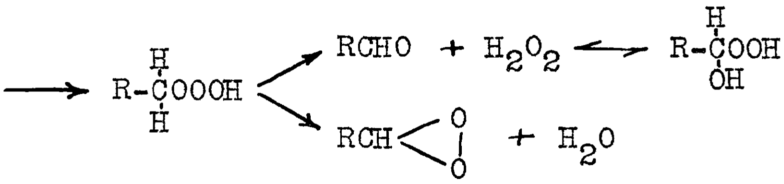


from which a chain is formed, in which

$e_n = e_1 + e_2 + \ldots\ldots\ldots\ldots\ldots$until the sum is so large that an explosion may occur. This chain is broken if an inhibitor molecule collides with the autoxidant and is itself activated and then either becomes oxidized by organic peroxides or oxygen, or combines with the autoxidants to form unstable complexes which may decompose to the original inhibitors.

In support of this theory he cites the following evidence: (1) Hydrogen peroxide has been detected, (2) Ozone produces similar effects, and (3) α - hydroxy alkyl hydroperoxides have been found in the reaction of aldehyde with H_2O_2 in an anhydrous medium. This is explained by the following specific reaction:

 (H is repelled)



One of the criteria of autoxidation reactions is the presence of an induction period. This corresponds to the time required to attain maximum velocity; the slow immeasurable rate increases and heat and/or light are evolved through the rearrangement and decomposition of the dative peroxides (cf. Matill - 205). Chain propagation is often enhanced by the induced oxidation of accelerators. Chemiluminescence has been observed in the oxidation of white phosphorus, formaldehyde, organic magnesium halides, and thiophosphonyl fluorides, but never in the oxidation of fatty acids or oils. Structure often plays a role in oxidation susceptibility; free hydroxyl groups usually have a retarding effect and end double bonds are less reactive than internal ones (cf. Kuhn and Meyer - 206.)

There are two classes of reactions, namely reversible and irreversible. Drying oils and hydrocarbons belong to the latter group and probably possess many similarities. Excellent reviews on the oxidation of hydrocarbons are given by Egloff and his co-workers (207). They postulate a chain mechanism with the intermediate formation of peroxides and aldehydes. Aldehydes, steam, oxides of carbon, and peroxides have been detected. The hydroxylation theory of Bone has received wide acceptance. A well-defined induction period is shown by ethane; this period is greatly shortened by the one per cent addition of acetaldehyde and initial increases in pressure, but is decreased by increasing the concentration of oxygen. Organic peroxides have been detected from the combustion of pentane, hexane, octane and gasoline. These peroxides, ROOCHOHR', liberate hydrogen when treated with strong alkali. The probable oxidation mechanism of hydrocarbons is the following:

$$H_3CH \xrightarrow{\text{activated}} H_3C:\rightarrow H$$
$$H_3CH \xrightarrow{\text{dissociate}} H_3C. + H.$$

$$H_3C:\rightarrow H + O_2 \rightarrow H_3COOH$$

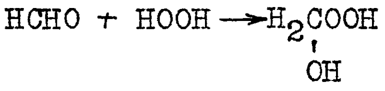
$$2H_3C. + O_2 \longrightarrow H_3COOCH_3$$

$$2\ H. + O_2 \longrightarrow HOOH$$

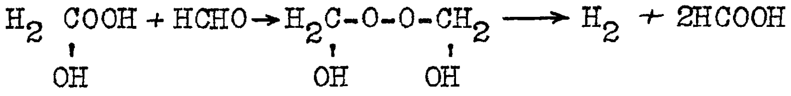
$$H_3COOH \longrightarrow HCHO + H_2O$$

$$H_3COOCH_3 \longrightarrow CH_3OH + HCHO$$

$$H_3COOH + HCHO \rightarrow H_3COOCH_2OH \rightarrow CH_3OH + HCOOH$$
$$H_3COOCH_2OH \rightarrow H_2 + HCHO + HCOOH$$



$$HCHO + HOOH \rightarrow \underset{\substack{|\\ OH}}{H_2COOH}$$



$$\underset{\substack{|\\ OH}}{H_2\ COOH} + HCHO \rightarrow \underset{\substack{|\\ OH}}{H_2C}-O-O-\underset{\substack{|\\ OH}}{CH_2} \longrightarrow H_2 + 2HCOOH$$

Coffey (208) oxidized thin films of fatty acids at 100°C. in a sealed apparatus containing oxygen. Solid caustic potash and concentrated H_2SO_4 were used to absorb the volatile products. He found that (1) the acids absorbed 30.1 per cent oxygen, (2) the reaction is unimolecular and non-reversible, (3) peroxides are formed in the early stages since (a) the oxygen absorption is approximately two atoms per double bond and (b) the oil liberates iodine from potassium iodide, (4) hydrogen peroxide is formed since the volatile products liberate iodine from potassium iodide, (5) the CO_2 produced apparently comes from the carboxyl group, and (6) the oxygen absorption is 25 per cent higher than theoretical, due to the production of volatile products.

The oxygen absorption of fatty acids has also been observed by Bauer (209), Petrov (210) and Long (211, 212). Bauer found that linolenic acid absorbed four atoms of oxygen in a bimolecular reaction. Petrov and Sokolov observed a weight gain of 16.24 per cent in the drying of linseed fatty acids; the oil only gained 7.8 per cent. Long and Chataway (211) observed that the free fatty acids of linseed oil absorb oxygen faster and in more quantity than the oil itself. Long and McCarter (212) found similar results.

In studying the blowing of linseed fatty acids, Taylor (213) observed that they react at a slower rate than the oil but at a greater rate than the methyl and ethyl esters. The acids darken considerably but do not gel. This was confirmed by Bradley (214), who explains this non-gelation on the basis of his functionality concepts (cf. Polymerization).

Eibner and Jung (216) studied the drying of α-linoleic, α-linolenic, α-eleostearic and clupadonic acids. Linoleic dries slowly to a film; it has a maximum weight increase in 14 days, shows no color or softening in one year and turns dark red with evolution of gas when heated. Linolenic acid dries in 8-10 days, is more yellow in winter than in summer, browns at 100°C., has a tougher film, turns red-brown at 200° C. Eleostearic acid dries in 6-8 days, is less yellow than linolenic acid, but yellows when heated. Clupadonic acid dries in three days, turns brown at room temperature and is the least stable of all towards water. Eibner concludes that oxynic acids, which do not fully ripen due to the absence of glycerol, are present in the film.

Skellon (217) studied the oxidation of oleic acid by gaseous oxygen with and without catalysts. Oleic is known to oxidize first to isomeric 9,10 dihydroxy stearic acids and finally to a mixture of azelaic, suberic, oxalic, nonoic and octoic acids. Edmed considers the oxalic, as a product from the chain oxidation which produces nonoic acid. Lapworth considers it the main product of splitting. Lewkowitsch passed air through oleic acid for ten hours and determined six per cent oxidized acids in the product. Skellon considers that the oxygen adds to the double bond to form a peroxide-oxido complex, that CO_2 is evolved, and that hydroxylated acids form and lose water to form lactones. At 100°C., he obtained nonoic acid, 9, 10 dihydroxy stearic acid (m.p. 132°), hydroxylated acids, iso-oleic acid and traces of formic, oxalic and acetic acids. Two to three oxygen atoms add per molecule and much less than one carbon atom is destroyed. Catalytic oxidation at 120°C. using a trace of blown whale oil, yielded different yields of the above acids and in addition, some 9,10 dihydroxy stearic acid (m.p. 95°) but no nonoic acid was produced.

Franke (218) found that linoleic acid reacts faster in basic solvents than in neutral ones. Horio and Yamashita (219) showed that mercury lamp exposure catalyzes the later drying of fatty acids and oils. Täufel and Scuss (220) determined the peroxide content, Kreis reaction and oxygen absorption of oleic and linoleic acids. The autoxidative tendency of the latter is disproportionately large relative to the former. Light has a definite effect on these variables.

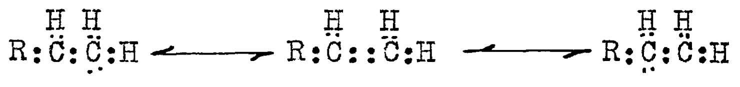
Hinsberg and Holland (221) studied the autoxidation of linoleic and linolenic acids in buffered solutions. The rapidity of methylene blue reduction and oxygen absorption increases with the number of double bonds. These acids produce reducing substances, probably aldehydes and ketones.

Hamilton and Olcott (222) determined the oxygen absorption of oleic acid and distribution of oxygen among the products of oxidation, including H_2O, CO_2, CO, OH, peroxide and CHO compounds. Oleic acid absorbs 4 atoms of oxygen per mole and loses one molecule of water. The destruction of the double bond is faster than a simple unimolecular reaction.

Franke and jerchel (222) studied the autoxidation of oleic, linoleic, linolenic and ricinoleic acids. The second and third acids absorbed oxygen faster and in larger amounts than the other two. Using one per cent $Co(NO_3)_3$ as a catalyst, they found that oleic and ricinoleic acids show a rapid decrease in the peroxide-oxygen absorption ratio with increasing oxygen absorption; the iodine value parallels the absorption up to 25 per cent absorption and then decreases slowly. The iodine values for linoleic and linolenic acids fall proportionately up to 60 per cent absorption and thereafter fall much slower. The individual double bonds of a polyunsaturated acid oxidize at different rates and the resulting peroxides, which decompose to α-hydroxy ketones, have different stabilities.

II. Autoxidation and Polymerization

According to Milas (199), the autoxidation of unsaturated compounds leads to peroxides which polymerize in some manner. Morrell and Marks (223) state that oils polymerize through the dative peroxides, Standinger believes that monoxides, formed from the monomer peroxides, lead to polyoxides; this was never substantiated. Milas suggests the following schemes of direct polymerization of unsaturated molecules:



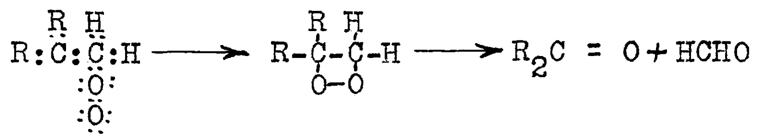
$$R:\overset{H}{\ddot{C}}:\underset{\cdot\cdot}{\overset{H}{C}}:H \longleftrightarrow R:\overset{H}{\ddot{C}}::\overset{H}{\ddot{C}}:H \longleftrightarrow R:\underset{\cdot\cdot}{\overset{H}{C}}:\overset{H}{\ddot{C}}:H$$

II I III

where II and III are the active autoxidants.

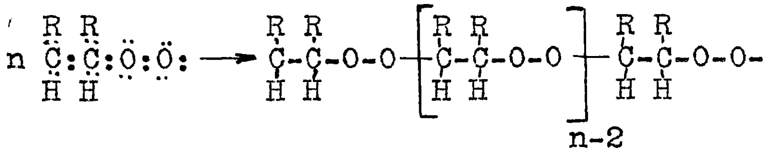
These unsaturated compounds add $\underset{\cdot\cdot}{\ddot{O}}:\underset{\cdot\cdot}{\ddot{O}}:$ to form dative peroxides which may either (a) rearrange to peroxides which break down and liberate energy, or (b) polymerize or (c) react with active unoxidized molecules to give mixed polymers and excess energy, which activates other molecules.

(a) Unsymmetrical structure:



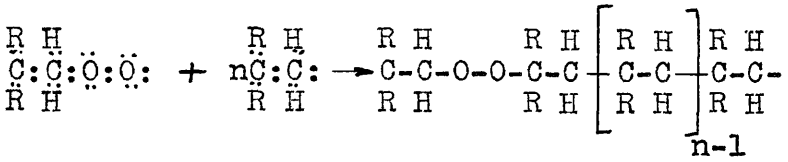
$$R:\overset{R}{\ddot{C}}:\underset{\substack{:\ddot{O}: \\ :\ddot{O}:}}{\overset{H}{\ddot{C}}}:H \longrightarrow R-\underset{O-O}{\overset{R\ \ H}{C-C}}-H \longrightarrow R_2C = O + HCHO$$

(b) Symmetrical structure: (drying oils)



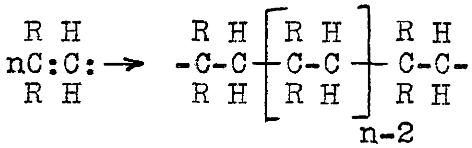
$$n\ \underset{H}{\overset{R}{\dot{C}}}:\underset{H}{\overset{R}{\dot{C}}}:\ddot{O}:\ddot{O}: \longrightarrow \underset{H}{\overset{R}{C}}-\underset{H}{\overset{R}{C}}-O-O-\left[\underset{H}{\overset{R}{C}}-\underset{H}{\overset{R}{C}}-O-O\right]_{n-2}-\underset{H}{\overset{R}{C}}-\underset{H}{\overset{R}{C}}-O-O-$$

(c) Mixed polymers:



$$\underset{R\,H}{\overset{R\,H}{\ddot{C}:\ddot{C}}}:\ddot{O}:\ddot{O}: + n\underset{R\,H}{\overset{R\,H}{\ddot{C}:\ddot{C}}}: \rightarrow \underset{R\,H}{\overset{R\,H}{C\text{-}C}}\text{-}O\text{-}O\text{-}\underset{R\,H}{\overset{R\,H}{C\text{-}C}}\left[\underset{R\,H}{\overset{R\,H}{C\text{-}C}}\right]_{n-1}\underset{R\,H}{\overset{R\,H}{C\text{-}C\text{-}}}$$

(d) Direct polymerization of activated compounds:



$$n\underset{R\,H}{\overset{R\,H}{C:C}}: \rightarrow \text{-}\underset{R\,H}{\overset{R\,H}{C\text{-}C}}\left[\underset{R\,H}{\overset{R\,H}{C\text{-}C}}\right]_{n-2}\underset{R\,H}{\overset{R\,H}{C\text{-}C\text{-}}}$$

Goldschmidt (224) measured the oxygen absorption, iodine number and peroxide value of linolenic acid. The sum of the latter two values equalled the iodine value of the original oil, from which he states that only peroxides are formed and polymerization accurs only through oxygen bonds.

Morrell (225) examined crystalline β-eleostearin from irradiated tung oil. When this is oxidized there are marked differences in the activity and character of the peroxide. The remote double bond position is basic and the near one is acidic. Nonpolar solvents such as CCl_4 and benzine, require an induction period, whereas glacial acetic acid gives a more rapid effect. He concludes that associated molecular aggregates are formed in the benzine solution, while a peroxide of dimeride character is formed in the acetic acid solution.

OXIDATION OF SYNTHETIC ESTERS

I. Autoxidation

Most of the discussion of the previous section applies equally well to this field. Certain modifications must be made when the condensed alcohol originally contained more than one hydroxyl group; these will be discussed in the succeeding sections.

Lea (226) oxidized methyl oleate with hydrogen peroxide in acetic acid solution. As a by-product, expecially at low temperature, he obtained an oily, oxidized ester of lower iodine number than the original ester. This product gives the peroxide test and evolves considerable gas when heated to 100°C. Thereafter it no longer gives a peroxide test but its iodine value has greatly increased. This indicates a loose union of oxygen with the double bond of the oleate. Hilditch (227) does not consider the reaction strictly autocatalytic because the oxygen absorption-time curves do not show a true inductive period. Distillation analysis of the fatty acid esters shows that they absorb oxygen immediately.

Petrov and Sokolov (210) oxidized the fraction of the ethyl esters of the linseed oil fatty acids which distilled between 210°-230°C. These purified esters gained 24.9 per cent in weight but later lost some of this. They formed semi-solid polymers with no evidence of skinning.

Long and McCarter (212) prepared the following esters of the free fatty acids of linseed oil: (1) methyl and (2) pentaerythritol ester. They studied the effects of driers, temperature, inhibitors, complexity of molecule and acid value by means of the oxygen absorption of both the gel and the volatile products. The methyl esters absorb 30 per cent more oxygen than the oil, but no gel is produced. The erythritol ester gels very quickly and absorbs 29 per cent less oxygen than the oil. This supports Long's theory that gelation occurs when the size, polarity, complexity and free energy of the molecules reach a certain point; association occurs between polar molecules until the requisite complexity is attained. Taylor (228) blew the methyl, ethyl and pentaerythritol esters of the linseed fatty acids with air at 30-35°C. After 244 hours the latter formed a clear, dry, tack-free gel, which contained 21.1 per cent oxygen, dissolved in 50 per cent xylol and dried better than gelled linseed oil. The methyl and ethyl esters remained liquid, even after 672 hours blowing and absorbed the theoretical amount of oxygen.

Long, Kittelberger, Scott and Egge (229) studied the orientation of blown glycol and mannitol esters of the free fatty acids of linseed oil, by means of a Langmuir balance. Blowing these esters at 138°C. increases the required crumpling force because hydroxyl, carbonyl and similar groups have been introduced into the molecule and have increased its attraction for water.

Goldschmidt and Freudenberg (224) claim that peroxides are formed during the autoxidation of linolenic acid esters. Täufel and Scuss (220) prepared the ethyl and glycol esters of oleic acid. The peroxide and Kreis values fluctuate; the glycol ester shows the greater autoxidative tendency of the two. Hamilton and Olcott (230) studied methyl oleate, oleyl alcohol and oleic acid. The acid and ester both absorb four oxygen atoms per mole, while the alcohol absorbs five. Simultaneously, each loses one molecule of water. Secondary reactions probably occur since the destruction of double bonds is faster than a unimolecular reaction rate.

II. Autoxidation and Polymerization

Goldschmidt and Freudenberg (224) found that the sum of the iodine and peroxide values equalled the iodine value of the unoxidized methyl oleate. Therefore, only peroxides are formed and polymerization occurs only through the oxygen bonds.

Bradley (214) has applied his functionality and convertibility concepts to the oxidation of synthetic esters. He prepared the ethyl esters of linseed and tung oil acids and evaluated them with respect to their oxygen convertibility. The ability to undergo oxygen conversion is governed by the molecular structure of the reactants, requiring, as in the case of heat bodying, the presence of polyfunctional reactants, at least one of which must be more than bifunctional. As a secondary requirement, at least one of the reactants must contain functional groups which are capable of being activated and caused to react by means of oxygen. The drying process involves the transformation of these linear molecules into three-dimensional polymeric forms. The ethyl esters remained liquid because of their 2,2 functionality. Complex esters of the alkyd resin type air-dried to gels when either the alcohol or the acid had a functionality greater than two. Failure to air-dry was observed only in the case of the heat non-convertible systems. Similar results have been obtained by Drinberg (231) and Fonrobert (232). The former observed that (1) monohydric alcohol esters of drying oil acids are oxidizable but remain liquid and non-film-forming, (2) ethylene and propylene glycol esters form only soft, plastic coatings, also completely soluble in petroleum ether, and (3) polyhydric alcohols of three or more hydroxyl groups formed esters which dried to insoluble films. Fonrobert and Pallauf found similar results with respect to heat convertibility.

Vincent (233) studied the oxygen induced gelation of unsaturated polyesters, in particular, the polyglycol maleates. Linear polytriethylene glycol maleate is a viscous oil, which, when suitably promoted by a cobalt salt, commences to air-dry in about 5 hours to an infusible and insoluble film. A number of the ethylene glycols and glycerol esters of maleic, fumaric, citraconic and succinic acids were prepared and examined for heat and oxygen convertibility. Pure polytriethylene glycol succinate is non-convertible whereas the ester produced by adding 10 per cent maleic acid during the condensation is convertible. Vincent assumes that gelation of the linear polyesters results from the union of a number of chains with growth of a three-dimensional structure, such growth being through primary bonds and not by secondary association forces. Experiments indicate that this polymerization results in the formation of a dimeric cyclobutane ring rather than a Staudinger-type addition or the formation of a hydroaromatic ring through the union of the chains is necessary to produce gelation, as indicated by the mixed succinic-maleic esters. This is analogous to the observation of Staudinger and Hener (235). They found that 0.002 per cent divinyl-benzene was sufficient to yield an insoluble gel when copolymerized with styrene. Bromine absorption indicates that many of the double bonds have taken no part in the polymerization except in cases where small percentages of the active acid were copolymerized with large amounts of inactive acids (e.g. mixed maleic-succinic esters polymerized to gels which show no residual bromine absorption).

Bradley, Kropa and Johnston (234) also studied glycol polyesters of maleic and succinic acids. They determined the acid number, viscosity, refractive index and other properties of these esters. From the acid number they calculated the number of condensation units per mole of condensation polymer, and from this the average molecular weight and average chain length. The glycol succinates were used as standards to detect the amount and extent of addition polymerization that may occur during the condensation of glycol maleate. This addition polymerization, which may occur under the influence of heat alone, is strongly accelerated by extremely small amounts of oxygen. This action of oxygen is promoted by heat, light and certain chemical substances (e.g. driers). If the addition polymerization is retarded during the preparation of these polyesters, it is possible to carry the condensation reactions farther and to obtain products of lower acid number and viscosity than is otherwise possible. Under the influence of oxygen and ultraviolet radiation these condensation polymers can be converted to infusible, insoluble polymers, provided only that the condensation has initially progressed beyond the half-ester stage and has resulted in an ester which contains not less than two carbon-to-carbon double bonds per molecule. These observations support Bradley's theory of functionality as related to heat and oxygen convertibility (drying), through primary valence bonds.

III. Autoxidation And Association

Very little work has been done on the association theories of ester oxidation although, as we shall see, quite a good deal of investigation has been made on synthetic glycerides and natural oils.

Nevins (236) examined the behavior of mannitol tetralinoleate. This ester dries much faster than linseed oil. He determined the heats of combustion of the liquid and gel portions and also compared the heats of combustion of extracted and unextracted films. The extracted portion supports the theory that the liquid phase in the film is adsorbed and not mechanically entrained. The heats of combustion of the extracted phase and of the insoluble gel follow different paths, but approach the same value. This indicates that the liquid must acquire a certain complexity before gelation can occur. Solidification involves a chemical change of the adsorbed, oriented liquid phase. Since the heat of combustion of the film calculated from the percentage solid and liquid phases is greater than the determined value, an exothermic heat of adsorption is indicated. Ultimate analyses indicate that the solid phase has a definite composition and complexity. This complexity arises through colloidal association forces which aggregate the oxidized molecules of ester.

OXIDATION OF SYNTHETIC GLYCERIDES

Although the preparation of synthetic glycerides is still a major problem, as evidenced by the work of Long and his associates (229), some significant results have been obtained from oxidation experiments on these materials. Since they represent the basic units of drying oils, their behavior will give some insight into the mechanism of oil oxidation.

I. Autoxidation

Täufel and Scuss (220) determined the peroxide value, Kreis reaction and oxygen absorption of triolein. Its autoxidative tendency was found to be less than that of the acid or the glycol or ethyl esters.

Long and McCarter (212) prepared the triglycerides of oleic, linolenic and eleostearic acids. These were blown with oxygen up to the gelation point and the effects of temperature, driers and inhibitors were studied. The oxygen absorption of the gel and of the volatile products was measured. The oleic triglyceride absorbs more oxygen and gels much slower than the other two glycerides. Trilinolenic glyceride gels much sooner than linseed oil, but it absorbs about the same quantity of oxygen. Results indicate that oxidation is a contributory effect in aiding the attainment of a definite molecular size, polarity and complexity which is necessary for gel formation. The association appears to be through forces similar to crystallization forces, but weaker in their nature.

In their orientation studies, Long and his associates (229) prepared and studied the mono-, di- and triglycerides of stearic acid and of the mixed fatty acids of linseed oil. These samples were blown at 138°C. and the areas and crumpling forces were determined for thin films on water. The results obtained showed an increase in crumpling force due to the blowing action. This indicates that polar groups - hydroxyl, carbonyl, etc. - have been formed during blowing; such groups would increase the attraction of the oil molecule for the water and thus increase the actual crumpling force.

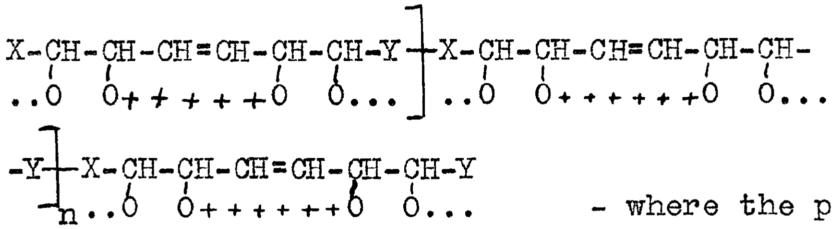
Scheiber (237) prepared the triglyceride of octadecadiene 9,11 acid-1, and prepared films containing (a) cobalt drier and (b) lead and manganese drier. These films do not yellow in two years when kept in a dessicator, but do so in a few months when exposed to the laboratory atmosphere. Scheiber ascribes this yellowing to an oxidation promoted by water. The subsequent bleaching action of strong light is a reduction process.

II. Autoxidation and Polymerization

Bradley (214) applies his convertibility and functionality concepts to the oxidation of synthetic glycerides. He prepared the mono- and diglycerides of the acids of tung oil and linseed oil. The diglyceride of the tung oil acids formed partially converted films; slightly tacky, increasing in tackiness with elevation of temperature, but not fusing; softened but not dissolved by acetone. The other esters formed only soft, tacky coatings which dissolved in acetone and melted below 100° C. The partial conversion of tung diglyceride may be due to the proportion of triglycerides or polyglyeerides present in it or to the development of a slightly greater degree of functionality than is normal through activation and reaction of additional points of unsaturation. The behavior of the other glycerides is strictly in accord with his theory of drying which is discussed in detail elsewhere.

Staudinger (238) proposes a primary polymerization of peroxides to polyoxides of the styrene type linear structure, viz. -

$X = CH_3(CH_2)_3 \qquad Y = (CH_2)_7\ COOH$



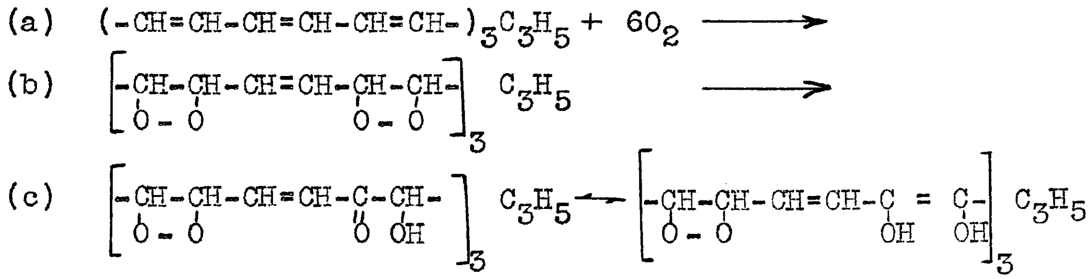
$$\mathrm{X{-}\underset{..O}{CH}{-}\underset{O+\,+}{CH}{-}\underset{+}{CH}{=}\underset{+}{CH}{-}\underset{+O}{CH}{-}\underset{O\ldots}{CH}{-}Y}\Bigg]\mathrm{X{-}\underset{..O}{CH}{-}\underset{O+\,+}{CH}{-}\underset{+\,+}{CH}{=}\underset{+}{CH}{-}\underset{+O}{CH}{-}\underset{O\ldots}{CH}{-}}$$

$$\mathrm{{-}Y}\Bigg[\mathrm{X{-}\underset{..O}{CH}{-}\underset{O+\,+}{CH}{-}\underset{+\,+}{CH}{=}\underset{+}{CH}{-}\underset{+O}{CH}{-}\underset{O\ldots}{CH}{-}Y}\Bigg]_n$$

- where the polarity of the near end of the polymer is greater than that of the far end.

III. Autoxidation and Association

Morrell and Marks, in a series of papers (239), studied the oxidation of the crystalline glyceride of -eleostearic acid. They isolated a product containing one peroxide group, one hydroxyl group, one carbonyl group and one carbon-carbon double bond. Saponification gave twice the glyceryl value, thus indicating fission of the molecule at some other point. Methylation with methanol and gaseous HCl yielded a keto-hydroxy peroxide ester and a keto-methoxy peroxide ester, as follows:



(a) $(-CH=CH-CH=CH-CH=CH-)_3C_3H_5 + 6O_2 \longrightarrow$

(b) $\left[\begin{array}{l}-CH-CH-CH=CH-CH-CH- \\ \;\;O-O \qquad\qquad\quad O-O\end{array}\right]_3 C_3H_5 \longrightarrow$

(c) $\left[\begin{array}{l}-CH-CH-CH=CH-\overset{}{C}-CH- \\ \;\;O-O \qquad\qquad\quad \overset{\|}{O}\;\; OH\end{array}\right]_3 C_3H_5 \longleftarrow \left[\begin{array}{l}-CH-CH-CH=CH-C = C- \\ \;\;O-O \qquad\qquad\quad OH \;\; OH\end{array}\right]_3 C_3H_5$

The one product is insoluble in petroleum ether and is associated, giving molecular weights varying from 2114 in benzine to 444 in acetic acid. The other product is soluble in petroleum ether and gives normal molecular weights varying from 440 to 370 in different solvents. In the former case, glacial acetic acid combines with the molecule and lowers the iodine value by causing dispersion at the expense of the double bonds. The high iodine values of oxidized oils may be due to structures such as (c), which develop a double bond through ketol-enol isomerism.

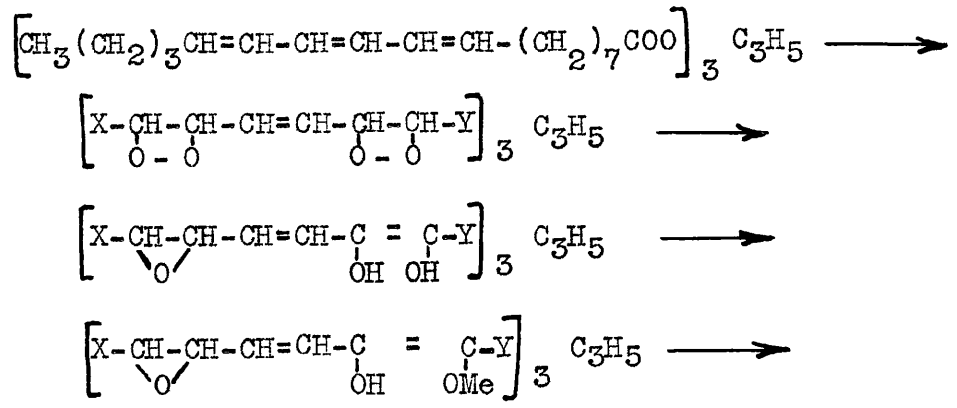
Piperidine formed an additive compound on the solid gel and split the molecule. The remote moloxide group is "basic" in nature, stable in the presence of acids but split by alkalis into two aldehyde groups. On the other hand, the near moloxide group is "acidic", forms colored salts and shows ketol-enol isomerism. Some of the conclusions reached by Morrell and Marks may be summarized as follows:

(1) The maximum number of methoxyl groups which can be introduced is two.

(2) Methyl ricinoleate does not methylate; the methyl ester of an acid isomeric with linoleic acid is obtained.

(3) Two isomeric oxidized esters are obtained; have different powers of methylation and different behaviors toward alkalis.

(4) $KMnO_4$ oxidizes the methyl esters to valeric acid and a 13 or 14 carbon acid, which decomposes into azelaic acid and traces of oxalic and glyoxylic acids, as follows:

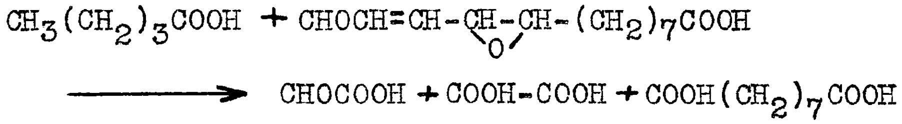


$$\left[CH_3(CH_2)_3CH=CH-CH=CH-CH=CH-(CH_2)_7COO\right]_3 C_3H_5 \longrightarrow$$

$$\left[X-\underset{O\,-}{CH}-\underset{O}{CH}-CH=CH-\underset{O\,-}{CH}-\underset{O}{CH}-Y\right]_3 C_3H_5 \longrightarrow$$

$$\left[X-\underbrace{CH-CH}_{O}-CH=CH-\underset{OH}{C}=\underset{OH}{C}-Y\right]_3 C_3H_5 \longrightarrow$$

$$\left[X-\underbrace{CH-CH}_{O}-CH=CH-\underset{OH}{C}=\underset{OMe}{C}-Y\right]_3 C_3H_5 \longrightarrow$$



$$CH_3(CH_2)_3COOH + CHOCH{=}CH-\underbrace{CH-CH}_{O}-(CH_2)_7COOH \longrightarrow CHOCOOH + COOH-COOH + COOH(CH_2)_7COOH$$

(5) Hydrogen reduction with palladium adds two or four atoms. The minimum obtains when the gel has aged. The other two atoms are involved in changing the peroxide to a monoxide.

(6) The remote peroxide adds HI in a loose fashion and forms a monoxide.

(7) When the esters are distilled, valeraldehyde and an oil, which reduces Fehling's solution, $AgNO_3$ and Schiff's solution and reacts with p-nitro phenylhydrazine and with bromine in CCl_4, are produced. Polarity in the peroxide groups is indicated. The remote grouping is basic; the polarity of the near moloxide is shown by the low contact angle of the dry film towards water. Bases raise the contact angle through an internal orientation of hydroxyl groups; an angle less than 65° gives the film the power to condense water and cause blooming.

(8) Yellowing is a result of rupture of the remote moloxide group and the formation of colored salts at the near group due to its enol form.

(9) The central double bond is inert.

(10) Polymerization depends upon the forces of coordinate covalency. Gelation, through the strong associating power of the peroxide groups, especially the near one,

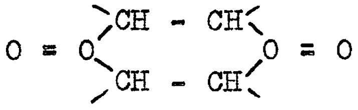
follows oxidation. In the experimental oxidations with dry oxygen gas, the glyceride in the remotest vessel gelled first; evidently the oxygen is activated.

Elm (240) studied the rate of oxidation of trilinolenic glyceride under partly controlled conditions, measured by the iodine number, gain in weight and peroxide, acid and ester values. During the first stage, peroxide groups are quantitatively formed to account for the decrease in ethanoid linkages. In the second stage, polymerization to association colloids occurs and a gel forms. This gel then ages and yellows by variations in the degree of association and not by oxidation. Morrell's ketoxy groups could not be identified.

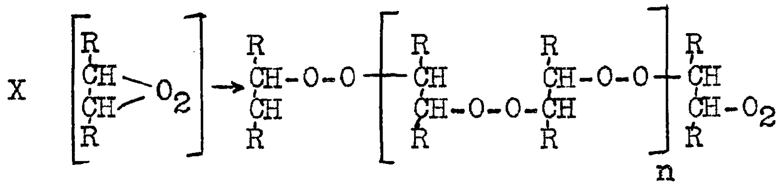
After the first peroxide-forming stage, the halogen addition decreases very rapidly but the peroxide content remains constant. Possibly unoxidized molecules are reacting to form two monoxide groups instead of one peroxide group. But a monoxide group should be capable of hydrolyzing to alcoholic groups, which might also cause yellowing. However, no alcoholic groups were detected. Therefore, either the α-monoxides are stable, an improbable property, or no monoxides are formed. Elm changed perbenzoic acid into a keto-form with three of the nine double bonds still intact, but this compound did not dry.

The acidity of the film increases with age, being 45 after 4 days, 73 after 60 days, and 192 after 2 years. Acid and ester values indicate that no hydrolysis occurs; the increased acid value is due to acidic decomposition products of low molecular weight. Tschirsch (241) regards hydrolysis as the cause of fat rancidity: $R\text{-}CH{=}CH\text{-}R' + O_2 \longrightarrow$ Peroxide which hydrolyzes to the monoxide and H_2O_2. The monoxide then polymerizes.

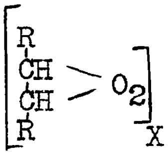
Swelling, viscosity and other properties indicate that colloidal polymerization must play a role, either by (1) condensation, (2) primary polymerization, or (3) association. The first is unlikely and has never been indicated. The second must take place in the presence of oxygen because no new carbon-carbon bonds or rings have been detected. In the presence of oxygen, Marcusson (242) postulates the formation of 1,4 dioxane rings such as -



But these have never been detected. True polymerization might occur to form the following structure:

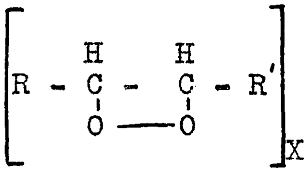


Or association could occur to form:



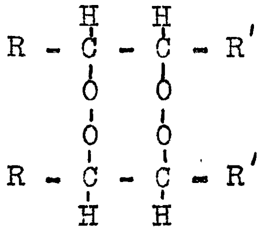
The principal difference between these two polymers will be their behavior towards solvents. Associated polymers are the same chemically as monomers because the primary valences are unchanged; furthermore, they will be affected by solvents. The results with acetone, benzene and carbon tetrachloride show an indefinite number of phases varying in their solubilities; some solvents actually depolymerize and then dissolve the molecules. Association polymers appear to be the more likely; the solid phase differs from the liquid only in the degree of association. Intramolecular polymerization is unlikely because the 120° angle between acid residues in the glyceride molecule would cause the polymer to be unstable, highly strained, compact and non-colloidal.

Long and Chataway (211) found that the glycerol esters of the unsaturated fatty acids gel when one double bond has changed to the peroxide form. Triolein oxidizes at about the same rate as linseed oil but requires 50 per cent more oxygen to gel. Trilinolenic glyceride requires the lowest amount of oxygen and gels very rapidly. The primary consideration seems to be the polarity and complexity of the molecule. The degree of unsaturation, oxygen and driers are secondary considerations. The final aggregation of these complex molecules is through secondary forces as -



$$\left[\begin{array}{ccccccc} & & H & & H & & \\ R & - & C & - & C & - & R' \\ & & | & & | & & \\ & & O & - & O & & \end{array}\right]_X$$

or through primary valence bonds forming -



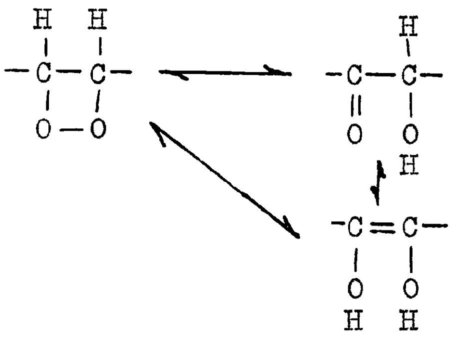
$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ R & - & C & - & C & - & R' \\ & & | & & | & & \\ & & O & & O & & \\ & & | & & | & & \\ & & O & & O & & \\ & & | & & | & & \\ R & - & C & - & C & - & R' \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Long, Rheineck and Ball prepared and studied trilinolenic glyceride. Air was blown through samples with and without driers; the volatile products were quantitatively analyzed; the oil was extracted with acetone to determine the percentage of liquid phase; ultimate analyses were made of the separated phases to see whether the change from liquid to solid took place only after the liquid phase had been oxidized to a certain composition. The gain in weight shows there is practically no induction period when 0.2 per cent drier is present. The net gain in weight corresponds to a take-up of 8.1 atoms of oxygen per molecule. When no drier is present, the net gain in weight up to the dry point is 19.25 per cent compared to 15 per cent with drier. Although the net change in weight is small after the glyceride is dry to touch, oxidation is proceeding at first rapidly, but the rate soon falls off to a very low value, and after some months the values for ultimate analysis remain sensibly constant. After this point further changes in the film are a matter of change of liquid phase into solid with little or no change in percentage of oxygen, rather than an oxidation. Further, the physical changes in the film which are considered as film failure occur long after gain in percentage of oxygen has ceased. This leads to the thesis that failure of films is not a matter of progressive oxidation catalyzed by metallic driers but of progressive change of liquid to solid by reactions of an "association" nature. Substances which decrease the velocity of this change will be of service in prolonging the life of films.

On the basis of the formation of a peroxide group at each double bond, one molecule of trilinolenic glyceride would take up 9 X 2 = 18 atoms of oxygen. If no volatile oxidation products were evolved, the solid oxidized product would contain 33.1 per cent oxygen.

Whole unextracted films of trilinolenic glyceride with drier equivalent to o.2 per cent metal (lead, cobalt, manganese) contained 31.55 per cent oxygen (exposed inside 288 days) and 32.27 per cent oxygen (exposed outside 164 days). These figures indicate that the composition of the entire unextracted film is nearly the same as that of the acetone insoluble (solid) phase and has apparently not only reached a maximum, but the maximum is nearly the theoretical maximum for this material.

The peroxides first formed during the early stages of oxidation undergo rearrangements involving formation of C = O and O - H groups as typified by the equation:



Gelation and film formation (drying) are ascribed to the attraction and association of these polar groups. If it is a matter of association (secondary attractions) rather than polymerization (primary valence change) or condensation, it should be possible to dissociate the films by use of solvents. Accordingly, the action of different types of solvents on films was studied. The results not only seem to strengthen the general premise of association but, on the basis that "like dissolves like," offer specific evidence of the existence of the polar C = O and O - H groups. The larger percentages of liquid phase were obtained with those solvents that contained C = O or O - H groups. Hydrocarbons and ethers extracted a smaller percentage of the film.

OXIDATION OF OILS

Much of the evidence, upon which the mechanism of drying oil oxidation is based, has been discussed in detail in the preceding sections. Particular emphasis should be placed on the results with synthetic glycerides because of their inherent similarity to the drying oil molecules.

In addition to this extensive evidence, numerous investigators have studied the oils directly or in connection with their acids and esters. These additional researches will be discussed in this section.

I. Autoxidation

Several investigators have only studied the property changes which take place during the oxidation of fatty oils, and have not concerned themselves with the theory behind these changes. Their results should, perhaps, be briefly summarized before proceeding with the theoretical investigations of other researchers.

Caldwell and Price (244) blew a 4500-gallon batch of rapeseed oil at 115° C. During the oxidation, the temperature rose to 150° C., the iodine number and heat of combustion decreased, and the acid number, saponification number, molecular weight, viscosity, refractive index and specific gravity increased. The saponification value increase is more than just an acid value increase; it indicates a decrease in the mean molecular weight of the acids during the blowing process.

Armani (247) oxidized cottonseed, animal-hoof and fish oils by filtered air at 93-98° C. for 500 hours. The color decreased and the molecular weight and viscosity increased. The acid number only slightly increased; the saponification number increased regularly and reached a maximum in fish oil at 247.5. The iodine number and mean molecular weight decreased regularly to minimums.

Yamaguchi (248) oxidized linseed oil and found that the absorption of oxygen was indefinitely unimolecular. Nakamura (249) studied the blowing of soybean oil with respect to (1) the estimation of active oxygen, (2) the effect of catalysts on the peroxide content, and (3) the rate of formation of peroxides. Active oxygen is not derived from the peroxides when heated at 200° C. for one hour. When the blown oil is heated, the peroxide content decreases 86.3 per cent, and the aldehyde content increases 24 per cent. Japanese acid clay, active carbon, and kieselguhr do not adsorb peroxides, but they do hasten their decomposition.

Salzenberg (250) blew linseed oil with dry oxygen at 20° C. for 18 hours. The color darkened slightly, but the viscosity showed only a slight increase. The same results obtained at 65° C. He noticed that break-free oil shows very little froth during blowing.

Long, Egge and Wetteran (251) studied the blowing of linseed and perilla oils. They determined the change in iodine number, molecular weight, hexabromide number, etc., and conclude that reactions occur which decrease the unsaturation disproportionately to the increase in molecular weight. In a later paper, Long (229) studied the orientation of blown oils on water surfaces by means of the Langmuir balance. Measurements of area and crumpling force indicate that blowing introduces polar groups (OH, CO, etc.) which increase the attraction of the water for the oil molecules.

Merzbacher (252) prepared and analyzed linoxyn. He found the following values: acid number=19, saponification number=291, iodine number=32.2, oxynic acids (insoluble in petroleum ether)=32.4 per cent. From saponifications and extractions, he detected the presence of glycerol, formic acid, propionic acid, caproic acid, pelargonic acid, azelaic acid, saturated acids of higher molecular weight, unsaturated higher fatty acids, acids soluble in petroleum ether, oxynic acids soluble and insoluble in water, and water-soluble organic compounds.

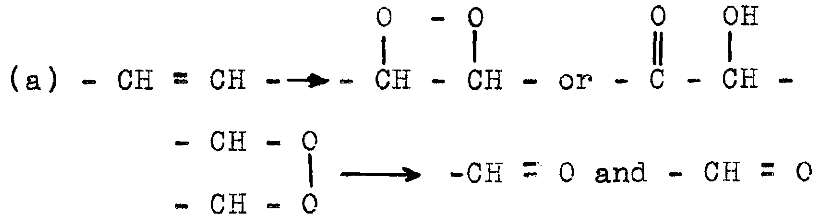
Gee (253) has applied monolayer techniques to the study of drying-oil problems.

Particular recourse to the work of Milas (199), in the section on fatty acid oxidation, should be made in order to review the fundamental ideas of autoxidative phenomena. Among the prominent early workers in this field should be mentioned Hazura (254), Kissling (255), Friend (256), Baly (257), Gardner (258), King (259), Salway (260), Orloff (261), and Rieche (262). Most of their work is antiquated and somewhat inaccurate, but they showed the pitfalls and broke the trail for those who followed.

Lippert (263) and Weger (264) were pioneers in exploiting the gain in weight method of measuring oxygen absorption. Genthe (265) definitely showed the antocatalytic nature of the oxidation reaction.

Jorissen (266) was one of the first to propose the formation of peroxides and their subsequent decomposition as the basic reactions of oil oxidation. Fokin (267) considers that the monoxide is the primary product, but his claims have been largely discounted.

Ingle (269) in comparing the oxygen absorption with iodine absorption found that the former was twice theoretical at its maximum value, i.e. $O_2 = I_2$ rather than $O = I_2$. He theorized the oxidation mechanism as follows:



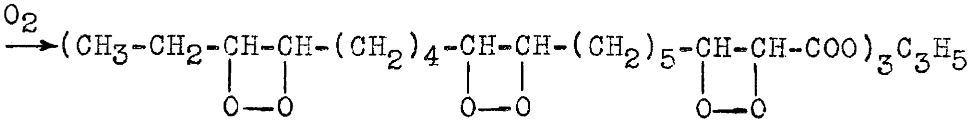
(a) $$-CH=CH \longrightarrow -\overset{O}{\overset{|}{CH}}-\overset{O}{\overset{|}{CH}}- \text{ or } -\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{CH}}-$$

(with $O - O$ joined above the first pair)

$$\begin{matrix}-CH-O\\ \quad\;\;|\\ -CH-O\end{matrix} \longrightarrow -CH=O \text{ and } -CH=O$$

(b) $(CH_3\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_4\text{-}CH{=}CH\text{-}(CH_2)_5\text{-}CH{=}CH\text{-}COO)_3C_3H_5$

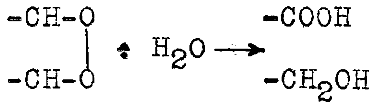
(L in olenin)



$$\xrightarrow{O_2}(CH_3\text{-}CH_2\text{-}\underset{O-O}{\underset{|\quad|}{CH\text{-}CH}}\text{-}(CH_2)_4\text{-}\underset{O-O}{\underset{|\quad|}{CH\text{-}CH}}\text{-}(CH_2)_5\text{-}\underset{O-O}{\underset{|\quad|}{CH\text{-}CH}}\text{-}COO)_3C_3H_5$$

$$\longrightarrow (CH_3CH_2CHO)_3 + 3CHO\ (CH_2)_4CHO + 3\ CHO\text{-}(CH_2)_5\ CHO +$$
$$(CHO\text{-}COO)_3C_3H_5$$

Oxidized oils have distinct acetyl numbers. Ingle explains this as due to hydrolysis of the peroxides to acid and alcohol groupings:



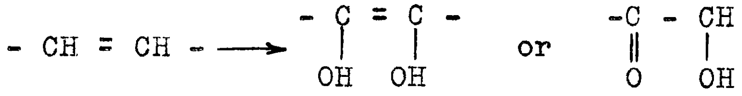
$$\begin{matrix}-CH\text{-}O \\ \quad\ | \\ -CH\text{-}O\end{matrix} + H_2O \longrightarrow \begin{matrix}-COOH \\ \\ -CH_2OH\end{matrix}$$

These groups would increase both the acid value and acetyl value and further could change to aldol derivatives - an experimental fact. Thus, both heat and moisture aid in decomposing and polymerizing the peroxide compounds.

In a series of papers, Ellis (270) studied the composition of linoxyn and its relationship to the mechanism of oil drying. A review of the earlier work on linoxyn justifies the hypothesis that it is a mixed glyceride composed of one linolenic acid radical and two linoleic acid radicals, which are autoxidized by the addition of seven mols of oxygen to $C_{57}H_{96}O_{20}$. Although he could not selectively extract a pure linoxyn of definite composition, he found that a solvent of 15 per cent ethyl alcohol and 85 per cent carbon tetrachloride was very effective. Linoxyn is either depolymerized or isomerized by the solvent. The minimum iodine value corresponds to the residual presence of one ethanoid linkage. Ultimates, saponification values and acid values indicate that the solvent has hydrolyzed the oxidized product and suggests the existence of isomeric forms. Thoroughly dried solvents yield the same compound as before. Linoxyn solutions reduce Fehling's solution and moist Ag_2O and turn starch-KI paper blue. Linoxyn appears to develop aldehydic structures on treatment with water as shown by their reaction with Schiff's reagent and with phenyl hydrazine. A hexanone ring structure with a number of hydroxyl groups is probable. When linoxyn is oxidized under dry conditions, no appreciable amounts of water-soluble acid products result. Thus, there is little justification for regarding more than a small portion of the volatile products as due to this primary oxidation process, and this small portion may represent a reaction secondary to that which forms linoxyn. Linoxyn is stable in dry oxygen, but in direct sunlight it absorbs oxygen, decomposes to a yellow, thick oil and carbon dioxide.

In a later article, Ellis cites evidence to show the presence of hydroxyl and carbonyl groups in linoxyn and its related oxyacids. Linoxyn contains 6-7 OH-groupings; acetylation, in the presence of pyridine, shows that these groups are alcoholic and not acidic. However, acidity develops in linoxyn through hydrolysis. The number of carbonyl groupings is fixed at six.

Ellis views the oxidation as a reaction in which hydroxy compounds are formed:



$$- CH = CH - \longrightarrow -\underset{\underset{OH}{|}}{C} = \underset{\underset{OH}{|}}{C} - \quad \text{or} \quad -\underset{\underset{O}{\|}}{C} - \underset{\underset{OH}{|}}{CH}$$

These groupings further may form closed ring structures or may decompose into simpler substances:

(a) $CH_3-(CH_2)_4-CO-CHOH-CH_2-CHOH-CO-(CH_2)_7COOH$

(linolic acid oxidation product)

$\longrightarrow CH_3-(CH_2)_4\ C(OH)\ CHOH - CH_2\ CHOH-CO - CH - (CH_2)_6COOR$

(b) $CH_3CH_2COH = COHCH_2COH = COH-CH_2-COH = COH-(CH_2)_7\ COOH$

(linolenic acid oxidation product)

$\longrightarrow C_2H_5CO-CHOH-CH_2-CH_2OH$ and

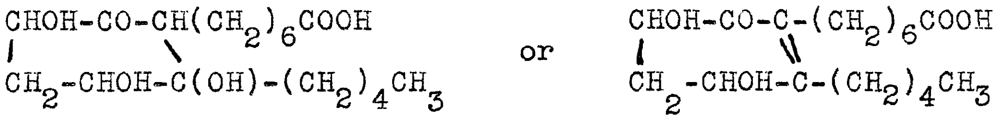
$HOOC-CH_2-CHOH-CO-(CH_2)_7\ COOH$

Glycol structures are improbable because of the presence of (OH) and (CO) groupings. Since dihydroxy maleic acid, $COOH-C(OH) = C(OH)-COOH$, is highly susceptible to hydrolysis, even in neutral solution, linoxyn probably has a similar hydrolysis to form either aldehydes or acids. The formation of aldehydes, acids and resins by moisture or alkali treatment of linoxyn has often been observed.

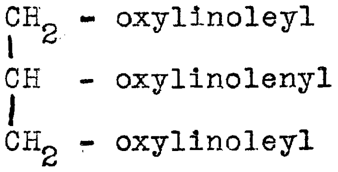
The enol form of oxylinolenic acid, $CH_3\left[CH_2C(OH)=C(OH)\right]_3(CH_2)_7COOH$, may partially exist in solution, but only the ketol form exists in the solid.

The slow action of solvents probably promotes this isomeric change. Polyphenols, which are believed to possess similar structures, are very good solvents for linoxyn. Hydrolysis should convert the ketol form to a monobasic acid glyceride, $C_{51}H_{86}O_{18}$; this compound has been isolated and analysis indicates that 2-3 H_2O have reacted.

Oxylinoleic acid is less negative than oxylinolenic acid, and would tend less to assume the enol form. Evidence indicates the presence of the 1,5 diketone, $CH_3(CH_2)_4COCHOH\ CH_2CHOHCO(CH_2)_7COOH$. This compound would tend towards ring formation either by prototropic movement or by the elimination of water, as follows:



There is little doubt of the existence of the latter compound in the saponification products of linoxyn and in crude oxylinoleic acid. The deficiency in the number of carbonyl groups in linoxyn may be explained by the isolation of a pale, yellow oil having the composition of cyclohexenediolone. Linoxyn is represented as the following structure:



CH_2 - oxylinoleyl
CH - oxylinolenyl
CH_2 - oxylinoleyl

Chatterji and Finck (271) attempted to measure the true oxygen absorption of linseed and cottonseed oils without the aid of a catalyst or spreading medium, and at the lowest possible temperature in order to minimize secondary reactions. They used a bubbler apparatus with oxygen, air, and oxygen-ozone mixtures. With linseed oil the induction period varied from more than thirty days at 18° C. to less than five days at 40° C. The oxygen absorption was 11.4 per cent for linseed oil, and 7.2 per cent for cottonseed oil; theoretical absorption (2I = 0) is 11-12 per cent. The oxygen absorption increased at higher temperatures.

Morrell (272) detected diperoxy linolenic glyceride in linoxyn. Ingle's triperoxy compound is never realized, but may be an autocatalyst in the reaction when no driers are present. The originally formed peroxides polymerize and decompose during the drying of the oil. In a very recent paper, Morrell (273) studied the methylation of 9 hydroxy, 10 keto- and 10 hydroxy, 9 keto-stearic acids as an aid towards understanding the reactions of oxidized oil molecules. The ketol group in the first instance can be methylated, but that in the second cannot. This may have bearing upon the structure of the oxyacids of linseed oil.

Coffey (274) oxidized linseed oil in a sealed apparatus, which absorbed the volatile products in concentrated H_2SO_4 and in solid KOH. The oil underwent a heterogeneous, non-reversible, approximately unimolecular reaction, which absorbed 28.7 per cent oxygen. In the early stages, peroxides are formed since the apparent oxygen absorption-iodine ratio is 1:1, and since the oil liberates iodine from KI solution. In the process, hydrogen peroxide is formed; the volatile products also liberate iodine from KI solution. The carbon dioxide loss balances the carboxyl content of the oil. Since the apparent oxygen absorption is 25 per cent higher than theoretical, Coffey believes that the early oxidation is autocatalytic, and that later an excess oxidation occurs. Glycerol has no effect in the oxidation because it can be quantitatively recovered.

Evans, Marling and Lower (275) found that the acid value of films containing cobalt acetate drier is an increasing function of the drying time and a logarithmic function of the drier concentration. If peroxides form, split to aldehydes and oxidize to acids, then the iodine number should be in inverse ratio to the acid number; this relationship is shown when cobalt, manganese and lead compounds are used as driers.

Hilditch (277) considers the early stages as the progressive formation of peroxides following the initial solution and adsorption of the gaseous oxygen in the oil. These peroxides probably rearrange, decompose and polymerize up to the gelation point. The reaction is not autocatalytic as shown by the true oxygen absorption curves and by the evidence that synthetic esters absorb oxygen immediately.

Petrov and Sokolor (278) oxidized linseed oil with driers, without driers and by blowing. Blowing produced a rapid oxidation to a viscous oil. With cobalt linoleate drier, an amount of oxygen was absorbed equal to 7.8 per cent gain in weight. In a later paper, Petrov and Kasterina (279) blew linseed oil at 50°-170° C. for 30-40 hours. The decrease in iodine value, the large production of hydroxy acids, and the differences between the saponification and acid numbers is cited as evidence of lactone formation.

Fuks (280) studied the rate of drying of linseed oil. He found the rate was independent of the film thickness within certain limits. After a certain thickness, the gel thickness does not increase and the oxygen absorption remains the same. Mathematically, W (the rate) $= dC/(b+C)$ where $C =$ concentration of oxygen, and b and d are constants. The rate in pure oxygen is only 3 per cent higher than that in air. He assumes two phases: (1) the addition of oxygen to the catalyst, and (2) the transfer of the oxygen in an activated state to the oil triglyceride.

Horio (281) investigated the oxygen absorption by photochemical means. When oxygen is bubbled through linseed and olive oils under the radiation of a quartz mercury arc, peroxides are formed. The rate of the linseed oxidation is independent of time, concentration and temperature, is proportional to the concentration of oil and to the square root of the light intensity. The rate of oxidation of olive oil decreased with time, but as in the linseed oil oxidation, chain reactions are involved. Working with Yamashita, Horio (282) found negligible changes in refractive index, acid number and iodine value of linseed oil exposed to the mercury arc lamp. However, when heated and oxidized, these exposed oils changed properties much faster than unexposed oils. The exposure forms considerable amounts of peroxide oxygen according to tests. The following mechanism is proposed:

$$\begin{aligned}
&A + hv \rightarrow A'\\
&A' + O_2 \rightarrow AO_2'\\
&AO_2' + A \rightarrow A' + AO_2\\
&AO_2' + M \rightarrow M' + AO_2\\
&M' + A \rightarrow A' + M
\end{aligned}$$

where A = oil molecule, and M = solvent molecule.

Aas (283) determined the change in iodine number in relation to the change in weight. In the early stages, there is a direct proportionality, but in the later stages the decrease in iodine value is not accompanied by a corresponding increase in weight. The early stage represents direct absorption of oxygen at the ethanoid linkages; the number of atoms of oxygen per double bond varies for different oils: linseed = 1.81, whale = 2.18-2.03, herring = 1.87-1.96, olive = 3.65-3.86, and soybean oil = 3.93.

Behrer (285) emphasizes the importance of the autoxidation of drying oil films as a process whereby: (1) molecular linkages responsible for elasticity are attacked, and (2) acids are produced and give rise to unfavorable effects on properties such as adhesion.

Iwai (286) gives a mathematical expression for the absorption of oxygen by drying oils. He considers this absorption as a simple diffusion of oxygen into the oil film. If no drier is present, there is an induction period followed by a logarithmic diffusion curve.

II. Autoxidation and Polymerization:

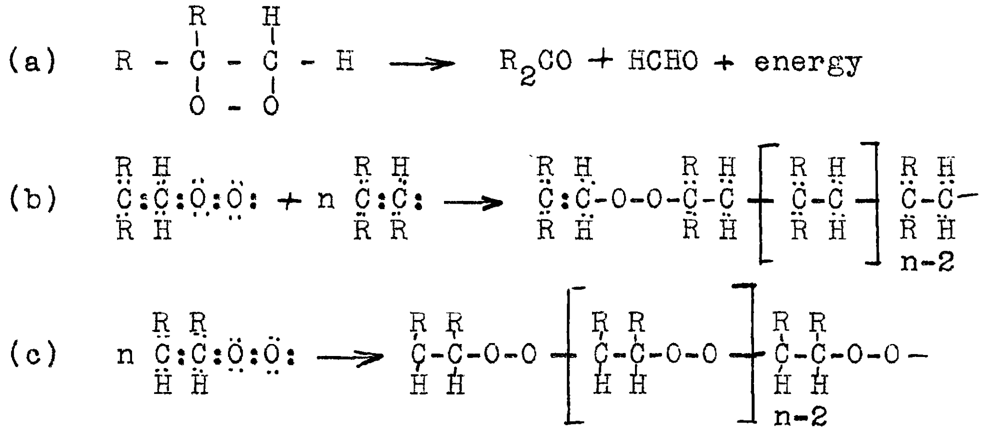
Milas (199) has briefly summarized the evidence in this field. Autoxidation precedes the polymerization which may be of several types: (1) through or of the dative peroxides, (2) direct polymerization of activated molecules, and (3) decomposition to monoxides which aggregate to polyoxides. The latter idea has been proposed by Fahrion (287) and by Staudinger (288).

Fahrion (loc. cit.) believes that peroxides are formed which undergo intramolecular change, forming ketol-enol systems, which condense through the elimination of water to form linoxyn.

Staudinger (loc. cit.) investigated the ozonides of dicyclopentadiene and dihydrodicyclopentadiene. The first compound in acetic acid yielded a diozonide which was monomolecular, soluble and easily split; when treated in CCl_4, an insoluble, stable ozonide polymer was produced. The second compound gives similar results. Both products result from a rearrangement of the primary product, but are not direct additions of the primary product; a mobility, similar to that of the primary moloxide of autoxidants, must be assumed. The final polymers are built up of oxides which join through the oxygen bonds.

Polymerization through the dative peroxides is upheld by many, among whom Milas (loc. cit.) and Morrell (289,290) are prominent. As early as 1918, Morrell favored polymerization subsequent to or simultaneously with the formation of dative peroxides. In a later paper, Morrell and Marks (290) showed that the grouping - C(OH) = C(OH) - is present in the oxidized forms of tung oil. The experimentally determined hydroxyl content confirms this mechanism. When methylated and vacuum distilled, the oxidized oil yielded an ester of a methoxy compound derived from a keto-alcohol, and an ester of a polymerized dihydroxy peroxide. The evidence suggests two types of peroxide: (1) an acidic type, and (2) a basic, less stable type which is probably involved in the earlier stages of the polymerization. Molecular aggregation proceeds from this keto-alcohol structure until the oil gels. A more detailed account of Morrell's work may be found in the section on the oxidation of synthetic glycerides.

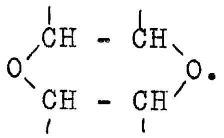
In the opinion of Milas (loc. cit.) dative peroxides are first formed; these either (a) rearrange to peroxides which break down and liberate energy, or (b) react with unoxided molecules to produce mixed polymers, or (c) directly polymerize. These various possibilities are illustrated as follows:



$$\text{(a)}\quad R-\underset{\underset{O\,-}{|}}{\overset{\overset{R}{|}}{C}}-\underset{\underset{O}{|}}{\overset{\overset{H}{|}}{C}}-H \longrightarrow R_2CO + HCHO + \text{energy}$$

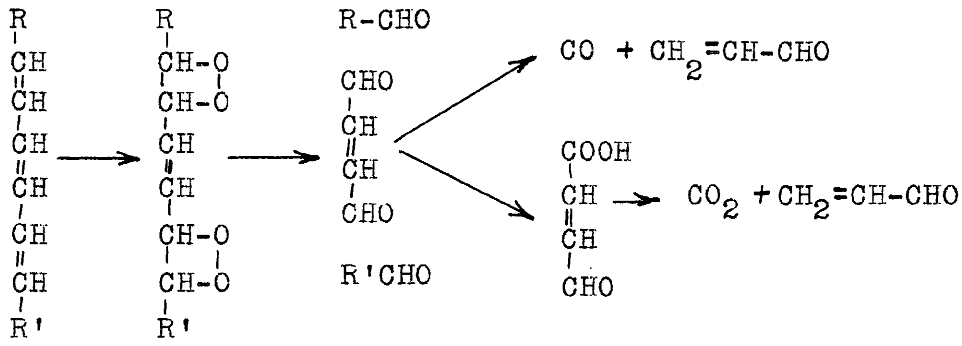
$$\text{(b)}\quad \underset{R}{\overset{R}{\ddot{C}}}:\underset{H}{\overset{H}{\ddot{C}}}:\ddot{O}:\ddot{O}: + n\ \underset{R}{\overset{R}{\ddot{C}}}:\underset{R}{\overset{H}{\ddot{C}}}: \longrightarrow \underset{R}{\overset{R}{\ddot{C}}}:\underset{H}{\overset{H}{\ddot{C}}}-O-O-\underset{R}{\overset{R}{C}}-\underset{H}{\overset{H}{C}}-\left[\underset{R}{\overset{R}{C}}-\underset{H}{\overset{H}{C}}-\right]_{n-2}\underset{R}{\overset{R}{C}}-\underset{H}{\overset{H}{C}}-$$

$$\text{(c)}\quad n\ \underset{H}{\overset{R}{C}}:\underset{H}{\overset{R}{C}}:\ddot{O}:\ddot{O}: \longrightarrow \underset{H}{\overset{R}{C}}-\underset{H}{\overset{R}{C}}-O-O-\left[\underset{H}{\overset{R}{C}}-\underset{H}{\overset{R}{C}}-O-O-\right]_{n-2}\underset{H}{\overset{R}{C}}-\underset{H}{\overset{R}{C}}-O-O-$$

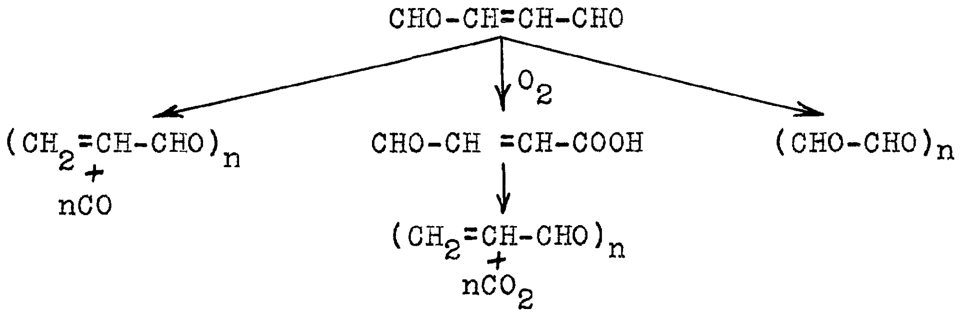
Some investigators, notably Eibner (291), Munzert, and Marcusson (242), consider that the peroxides polymerize to 1,4 dioxane rings. This viewpoint has been largely discredited because of the properties of the oil film (cf. Morrell and Marks - 239), and the absorption of two atoms of oxygen per ethanoid linkage (cf. Long and Chataway - 211). In a series of articles, Eibner and Munzert (292) investigated the properties of oxyns or oil films. They found no proof for the presence of glycerides of true hydroxy acids, but negative proofs were shown by the low acetyl number, the absence of water soluble acids, and the absence of crystallizable acids from the brown syrupy "oxy" acids. Evidence which they obtained points towards intramolecular polymerization coupled with extramolecular polymerization by oxidation to form dioxane rings,  The observed low content of active oxygen (1%-3%) favors the presence of monoxides rather than peroxides; evidently polymerization is greater than autoxidation. They found that molecular weight determinations depended upon the degree of dispersion, the concentration of solution, the solvent and the nature of the substance being examined. Natural drying shows a different type of polymerization than is met with in boiled oil drying; the latter is more complex because of rearrangements within the molecules of the fatty acids of the glyceride itself. The formation of stearic acid by the hydrogenation of the least dispersed portion of boiled oils proves the absence of dioxane rings in this case.

Elm (240) particularly concerned himself with the yellowing of oil films. He considers this color due to hydrolysis of moloxides, the rearrangement of the monoxides formed, and the polymerization of the final keto-product to the gel stage. The polymerization of aldehydes is also a factor in the color formation. Rheineck (294) proposes a similar mechanism.

The polymerization of aldehydes has furnished the basis for Salway's theory (295) of drying. He assumes the following structure and mechanism of oxidation for linolenic acid present in a glyceride molecule:



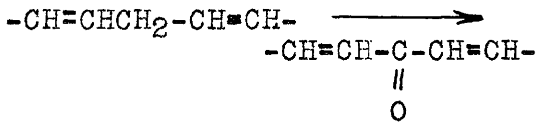
The central double bond is stable so that a dioxygenide is formed which ultimately decomposes to acrolein. Both the usual unconjugated linolenic acid and the conjugated form are considered present. Salway explains drying as a polymerization of acrolein. He detected acrolein qualitatively by the decoloration of bromine water, and quantitatively by the precipitation of silver acrylate. Rideal and Taylor (296) give a very similar scheme, but modify the action after the formation of



Blom (297) adopts a middle course and decides that the linking of individual glycerides may come through (1) carbon-carbon bonds in heat polymerization, (2) oxygen bridges in film formation, or (3) both linkages in simultaneous blowing and heating or in film formation from stand oil.

Hilditch (227) states that the oil molecules aggregate by means of a lateral build-up between molecules rather than a longitudinal aggregation as in the cellulose structure.

Scheifele (299) advanced the theory that film formation was entirely the result of the condensation of oil molecules containing conjugated double bond systems. Subsequently, Scheiber (298) developed this theory more fully. He states that the preliminary oxidation of all the drying oils - with the exception of tung and related oils - results in the formation of conjugated double-bond systems throughout the oil, and it is about these centers of activity that condensation and polymerization occur. The mechanism proposed for this reaction is:



$$-CH=CHCH_2-CH=CH- \longrightarrow -CH=CH-\underset{\underset{O}{\|}}{C}-CH=CH-$$

Conjugate systems, in general, show the following characteristic properties:

1. A conjugated system has a higher refractive index than that of a nonconjugated isomer.

2. A conjugated system has a lower heat of combustion than that of a nonconjugated isomer.

3. A conjugated system reacts with halogenating agents relatively slowly.

4. A conjugated system reacts readily with maleic anhydride, and, so far as is known, the nonconjugated system does not react.

Taylor and Smull (300) studied the changes in refractive index, heat of combustion, and iodine number resulting from the oxidation of linseed oil. In addition, the reaction of Diels and Alder involving maleic anhydride and conjugated compounds was applied to the oil in various degrees of oxidation. The oils used were alkali-refined linseed oils. Oxidation was carried out by bubbling air through the oil in glass percolators. The temperature was regulated by an electric resistance which was enclosed in glass and immersed in the oil. The results obtained showed that the property changes were in accord with the behavior of a conjugated system. The point at which the oil begins to exhibit reactivity with maleic anhydride coincides with the point at which other properties are changing rapidly. Iodine and acetyl value determinations were made to show that maleic anhydride does not react with hydroxyl groups, and that it has no iodine value of its own.

The postulates of Bradley (301) with regard to the drying mechanism of oils might be summarized as follows:

"1. The so-called drying of the drying oils and resins is but a physical transformation involving a conversion of these substances from an essentially linear structure to a three-dimensional polymeric form.

2. This physical transformation, as in any other conversion, requires that the interacting molecules be polyreactive, and that at least one of the reactants be polyreactive to the extent of 3 or more.

3. The mechanism of this conversion, as of any other conversion, is governed by the specific nature of the reactive or functional groups; it requires, in the case of the drying oils and resins, a plurality of groups which are capable of reacting with oxygen; or in any other case, it requires that particular form of matter or of energy by means of which we desire the ultimate conversion to be effected."

For a detailed account of his results and arguments, see the sections on the polymerization of oils, and the oxidation of synthetic esters.

In a later paper, Bradley, Kropa and Johnston (234) suggest that, during the oxidation of linseed oil, the formation of carbonyl or of other groupings involving the carbon-to-oxygen double bond, may, in conjugation with the remaining unsaturation of these oils, result in addition polymerization; hence, under the further influence of the degree of functionality, it may also result in conversion or drying to an insoluble, infusible gel. This accords with the views of Scheifele, Scheiber and Taylor, as outlined above.

Nauroy (302) studied the boiling of linseed oil in air. He concludes that the first stage involves intramolecular polymerization by means of condensation reactions.

The polar properties of oils are due to peroxides at the free double bonds on the external dimer surface.

III. Autoxidation and Association

Most of the work on the association or colloidal theories of oil oxidation has been done by Long and his associates. However, Wornum (303) has made some excellent observations on the types and properties of dispersed phases. His discussion includes both primary and secondary valence effects, among which he considers two aspects: (1) the manner of micelle formation, and (2) the spatial distribution of units and its relationship to phase stability (i.e. the sol-gel transformation). Details of his viewpoint may be found in the section on the polymerization of oils, and they will not be repeated here. Suffice it to say that he considers gelation as arising through oxidation which destroys the phase stability. The oxygen crosslinking is probably mainly by covalent bonds. Surface oxidation and setting results in adsorption by the liquid phase and swelling. In other words, micelles form through primary and/or secondary valence forces, and then these micelles undergo spatial distribution changes resulting in phase instability or gelation.

Chataway (304) studied the average rate of reaction of linseed oil oxidation at different temperatures, and the total volume of oxygen absorbed at the time of gelation. Above 100° C., gelation occurred immediately upon the formation of a certain minimum percentage of oxidized glycerides; at lower temperatures larger percentages were required. She agrees with Slansky (306) that the first stage is a chemical change to oxidized glycerides, and the second stage is a colloidal coagulation of these oxidized molecules dispersed in the non-oxidized or non-oxidizable molecules. In later work with Long (211), Chataway studied the rate of oxidation of linseed oil at 160° C. absorbing most of the volatile products in H_2SO_4 and soda lime, and on a glowing Pt wire. The rate decreases approximately as a straight line function of the degree of oxidation; the oil gels at 12 per cent oxygen absorption. Gelation is considered to occur when a certain size or degree of complexity or polarity is attained.

Long (306), in a talk before the Toronto Paint and Varnish Superintendents Club, discussed his views on oil oxidation as of that date. The induction period is a slow change period in which impurities are being eliminated; oxidation is playing a role in thin films, but its chemical changes are not evident as yet. Immediately following this slow period is a period of micelle formation in which individual molecules join together to larger structures until their complexity leads to colloidal properties. This aggregation is in a definite arrangement and results in a decrease in the unsaturation of the oil, even before viscosity and density show any real increases. The unstable, polar peroxides or their rearrangement isomers may undergo condensation reactions and other changes; no matter what mechanism is involved, the free energy is decreased and the complexity of the system grows until gelation occurs. Subsequently, this gel loses elasticity, cracks and fails, probably through a weakening in the free energy of the double bonds as they absorb the relatively inactive constituents during the sol-gel transition.

In a later paper, Long, Rheineck and Ball (243) reiterate the same ideas and show evidence for the effects of temperature, humidity, solid pigments and catalysts on the drying process. Oils dried at 7° C. and at 52° C. although the rates of drying and the weights of volatile products were quite different in the two cases; the mechanisms and final compositions are probably significantly different. Moisture definitely inhibited the drying of oils and paints; saturated air prevented any drying of oil films in a period of thirty days. A summary of their conclusions on the theory of oil drying is quoted as follows:

> "The first stage in the drying of linseed oil films is a matter of oxidation or, more generally, of making polar molecules. The mechanism of reaction in this stage is greatly influenced by factors such as temperature and humidity. High humidity greatly inhibits and modifies the reactions occurring.

> The second stage in the drying involves association of the polar molecules produced in the first stage to form the solid gel-like coherent structure of the film. Some further oxidation occurs after the oil has "set", but the film is soon oxidized to a stage corresponding to the addition of two oxygen atoms at each double bond, and the percentage of oxygen remains practically constant thereafter.
>
> The aging of films of linseed oil or of trilinolenic glyceride consists in a gradual transition of polar liquid phase to solid phase of substantially the same ultimate analysis. Embrittlement and failure of drying oil films is primarily a matter of reduction of the percentage of liquid phase to low values."

Long and McCarter (212) studied the effect of temperature, driers, inhibitors, degree of unsaturation, degree of complexity, and acid value on the rate of oxidation of linseed oil up to the point of gelation. They used the same apparatus as that used in the work of Long and Chataway (loc. cit.). They found that free fatty acids unite with linseed oil during oxidation at 160° C., thus increasing the complexity of the molecule and facilitating gelation. Esters more complex than glycerides (e.g. pentaerythritols) gelled much more rapidly and with less oxygen absorption than linseed oil or its glycerides; the reverse occurs in the cases of the ethyl and glycol esters. Furthermore, linolenic triglyceride takes up twice as much oxygen as its isomer, eleostearic triglyceride, before gelation. From 50%-85% of the oxygen absorbed up to gelation remains in the oil gel. The other 15%-50% appears in volatile oxidation products which contain 3.5%-5% of the carbon and hydrogen of the original oil. Long and McCarter conclude that gelation is a colloidal association process which depends on the size, complexity, polarity and free energy of the molecules. Oxidation is merely a contributory cause. They mention incidentally that primary valence aggregations may be involved, but are so weak that the bonds can be disrupted by solvents, oxygen and other means as easily as typical secondary valence bonds.

Chapin (309) found that oxidizing oils acquire polarity and tend to dip downwards, thus decreasing the surface tension. Later the surface tension rises to that of the saturated liquid because the double bond groupings dip below the surface. His work supports the views of Long and others (loc. cit.).

Scheiber (310) concludes that the oxidation of oils is a chemical-colloidal process in which chemical reactions are necessary to produce nuclei around which coagulation occurs.

In a series of articles, Auer (311) has proposed his gas coagulation theory of drying. An excellent summary of his results and ideas can be found in his most recent publication (312), from which I quote:

> "Fatty oils are isocolloids which form solid films in thin layers as a result of the action of gases.

In film formation the gases behave aselectrolytes in coagulating lyophobic colloids. A certain threshold concentration must be reached.

The coagulating gases are adsorbed by the films. Such adsorption is a secondary process and is not essential for film formation. If adsorbed oxygen is the coagulating gas, chemical processes may result, but such processes are not essential for film formation. The amount of adsorbed gas is unimportant in film formation.

The film formation - i.e., gas coagulation - occurs in the gas-liquid interface, and it may be influenced by certain active capillary additions. Etheric oils retard film formation and metal soaps accelerate it by sensitizing the colloidal system for the gas coagulation.

The action of driers is a parallel sensitizing action to that of accelerators in vulcanization.

Fatty oils may be separated into two phases by formic acid, and the dispersed phase is capable of forming jellies with the dispersion medium of the oil as well as with nonfatty dispersion mediums.

When electrolytes are dissolved by the acid of heat in fatty oils, they form reversible, fusible, and soluble gels.

Heat bodying, bodying by air blowing, film formation, and vulcanization are parallel processes, and the colloidal structures formed are physically and chemically similar in nature.

Fatty oils form various types of sols and gels. The gels may be classified as reversible and irreversible. Films, oxyns, factices, and heat-gelled oils are irreversible gels which are infusible and insoluble in organic solvents without decomposition."

In a later article, Bradley (313) criticizes Auer's work on the basis of his results and those of

Schmalfuss and Werner, who could not confirm Auer's experimental results. Slansky (314) also opposes these results because he could find no change in the chemical or physical properties of linseed oil as a thin film on glass in a 2 mm. vacuum. These films were unchanged after sixteen days' exposure at 20° C. in a well-lighted room. Freundlich (315) examined raw, blown and boiled linseed oils for light polarization, plasticity and ultramicroscopic particles, but he could not find any evidence of colloidal states. He likewise opposes the colloidal views of Auer and others (loc. cit.).

Excellent reviews on the subject of oil oxidation may be found in references 316 to 326 inclusive. Particular mention is due a book written by Eibner (326), which summarizes all the existing theories and evidence on the oxidation of drying oils. Rheineck (325) has made an excellent translation of most of Eibner's work.

CATALYSIS

I. Introduction

In a study of the action of heat and oxygen on natural drying oils, the role of pro- and anticatalysts is an important factor in determining both the rate of reaction and, to a lesser extent, the actual mechanism of the reaction. Of particular importance are the natural antioxygens in the oil and the prŏoxygens which are added to the oil. The nature and behavior of these substances will be the subject of the following discussion. General information on catalysis may be obtained in the works of Sabatier (327), Ipatieff (328), Rideal and Taylor (329), and Frolich (330).

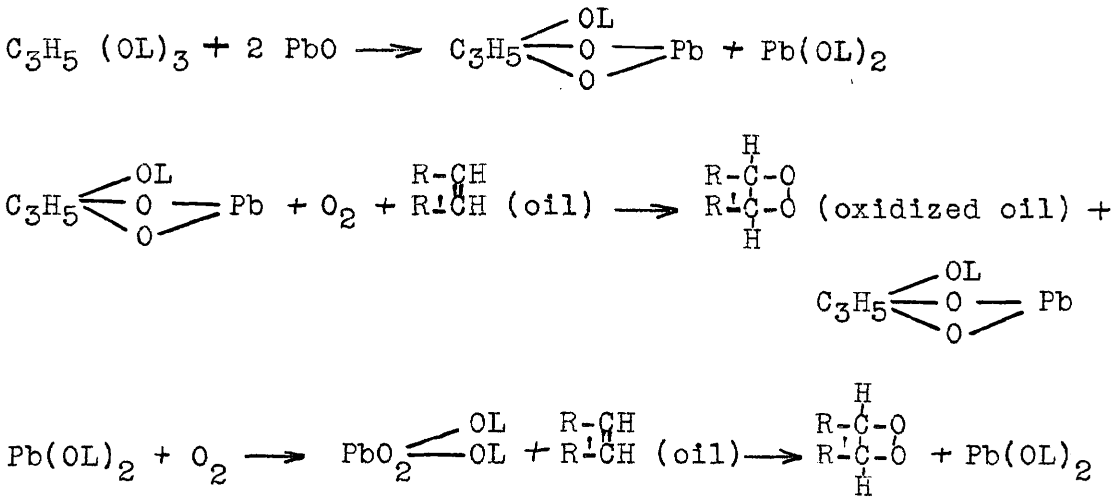
II. Prŏoxygens

There are two distinct schools of thought on the action of driers (i.e. pröoxygens) during the oxidation and polymerization of fatty oils. These theories may be classified as follows:

A. Intermediate compound theory (chemical).

B. Adsorption theory (physical).

Probably, one of the earliest exponents of the intermediate compound theory of drier action was Ingle (331). He proposed the following mechanism for the action of litharge during the drying of a fatty oil:



$$C_3H_5(OL)_3 + 2\,PbO \longrightarrow C_3H_5\begin{array}{l}OL\\O\\O\end{array}\!\!>Pb + Pb(OL)_2$$

$$C_3H_5\begin{array}{l}OL\\O\\O\end{array}\!\!>Pb + O_2 + \begin{array}{c}R-CH\\ \| \\ R'-CH\end{array}\text{ (oil)} \longrightarrow \begin{array}{c}H\\ | \\ R-C-O\\ | \quad | \\ R'-C-O\\ | \\ H\end{array}\text{ (oxidized oil)} + C_3H_5\begin{array}{l}OL\\O\\O\end{array}\!\!>Pb$$

$$Pb(OL)_2 + O_2 \longrightarrow PbO_2\begin{array}{l}OL\\OL\end{array} + \begin{array}{c}R-CH\\ \| \\ R'-CH\end{array}\text{ (oil)} \longrightarrow \begin{array}{c}H\\ | \\ R-C-O\\ | \quad | \\ R'-C-O\\ | \\ H\end{array} + Pb(OL)_2$$

The lead soap, by forming unstable intermediate complexes, is regenerated and can oxidize other oil molecules.

Rideal and Taylor (329) propose the following general scheme to illustrate drier action:

$A \text{ (oil)} + O_2 \longrightarrow A\,(O_2)$

$A + A\,(O_2) \longrightarrow 2\,A\,(O)$

$A\,(O_2) + B \text{ (inhibitor)} \longrightarrow A\,(O) + B\,(O) \longrightarrow A + B + O_2$

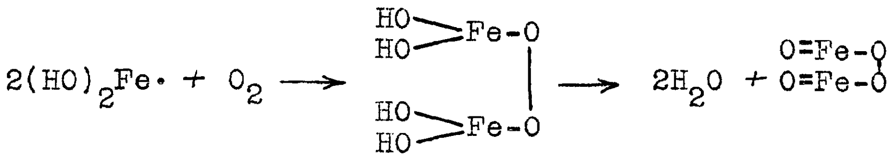
$A\,(O) + B \longrightarrow A + B\,(O)$

$A\,(O_2) + C \text{ (catalyst)} \longrightarrow A\,(O) + C\,(O)$

$A + C\,(O) \longrightarrow A\,(O) + C$

The catalyst acts by speeding up the decomposition of the peroxide oil molecules and by supplying oxygen to unoxidized oil molecules and being itself regenerated.

In his excellent review on the nature of autoxidation reactions, Milas (334) discusses the positive catalysis of these reactions by means of organic peroxides, ozonides, etc. and inorganic metals, salts and complexes. He proposes the following mechanism to explain the autoxidation of ferrous salts:



$$2(HO)_2Fe\cdot + O_2 \longrightarrow \begin{array}{c} (HO)_2{>}Fe{-}O \\ | \\ (HO)_2{>}Fe{-}O \end{array} \longrightarrow 2H_2O + \begin{array}{c} O{=}Fe{-}O \\ O{=}Fe{-}O \end{array}$$

The iron peroxide, being unstable, readily oxidizes the oil molecule and is itself reduced to a lower oxide.

Gee and Rideal (335) applied phase-boundary-potential methods to the study of the polymerization of monolayers of drying oils. They conclude that the catalyst forms a complex with the oil molecule in polymerization reactions, but oxidation catalysis does not require such complexes.

The physical or adsorption theory of drier action was suggested by Morrell (336) in 1920. Catalysis is an adsorption phenomenon in which the reaction velocity is proportional to the active volume of catalyst in the heterogeneous system and is influenced by the diffusion of reactants and products to the interface. Both a directive and selective adsorption are involved. The assumption is made that there is a chemical union between the surface of contact and the molecules similar to the atomic condition of a gas on an active surface (cf. Langmuir-337).

Schlich (338) cites the energetic catalytic action and the change of activity with degree of dispersion as evidence for the colloidal state and adsorptive character of driers. Evidence for colloidal dispersion is claimed from a study of various thinners on the basis of the volume required to flocculate zinc linoleate (339).

Slansky (340) states that the solid catalyst causes a condensation of the surface layer of molecules into atoms which become associated with certain molecules in the surface layer. A basic catalyst, such as PbO, draws the glyceride end of the oil molecule inwards and allows the unsaturated carbon chain to move outwards and be oxidized; on the other hand, a substance like carbon black causes adsorption at the unsaturated chain and thus retards oxidation.

Long (341) considers that the chemical theories are inadequate because driers are active even in the absence of air; in fact, driers probably catalyze the formation of a gel more than they do the oxidation of the oil molecule. Driers are colloidally dispersed in the oil and their essential molecule is similar to that of the ultimate oil molecule. These drier molecules tend to orient because of their polar character and act as nuclei for gel formation. However, attractive forces operating at certain definite points in the molecule and free energy changes are also involved. The larger amounts of drier result in a finer, faster-forming gel structure, but too large a percentage of drier induces premature gelation and a poor gel structure. Long, Scott, Kittelberger and Egge (342) studied the orientation of lead and manganese soaps by means of the Langmuir balance. Their curves indicate that these soaps are diglycerides which orient themselves on the water surface in a definite manner.

Wornum (343) applies similar concepts to explain the influence of driers on the phase stability (i.e. gelation). He considers that cobalt salts, which are strongly sensitizing, are adsorbed on the flocculate surfaces and modify the free energy of the particles in the disperse phase. The extent of the adsorption is proportional to the degree of dispersion of the drier, and is influenced by the nature and the size of the flocculates present.

Several investigators have introduced the idea of a pseudo-catalytic action in which the drier promotes the formation of the active catalyst, usually the oil peroxide.

Rhodes and van Wirt (344) believe that the presence of an induction period precludes the pseudo-catalytic nature of driers. Apparently some product, which promotes the union of oxygen with the oil, is formed during this period. The effect of metallic salts in accelerating the drying of oil is that these salts act as pseudo-catalysts to promote the formation of the autocatalysts and thus increase the rate of oxidation when it is first exposed to the air. The drier does not seem to have any effect on the amount of oxygen ultimately absorbed by the oil in drying. Pigments of metals which have a catalytic effect on drying of an oil also possess this effect, while pigments of other metals exhibit no effect, or some even an inhibiting effect.

The action of driers, according to Coffey (345), is considered to be autocatalytic because:

1. There appears to be no stoichiometric relation between the quantity of drier and the amount of oxygen absorbed.

2. The reaction curve appears to be logarithmic, of the form

$$k = \frac{m}{t_1} - \frac{1}{t_2} \log_e \frac{a}{a-x}$$

where: t_1 = period of induction

However, Coffey himself is of the opinion that although the drier may remain unchanged, it does not act as a catalyst in the strictest sense, because it obviously changes the course of the reaction. This is indicated by his work, which shows that if a drier is used, the oxygen absorption drops to around 12 per cent from the theoretical 15 per cent to 17 per cent, as calculated from the actual unsaturation of the oil.

Rogers and Taylor (346) studied the action of driers under controlled conditions of temperature, light intensity and humidity. Although the induction period is considerably shortened by cobalt linoleate and other siccatives, the general shape of the drying curves remains the same. This supports the theory that driers act as catalysts for the formation of autocatalytic substances formed during the oxidation.

As the concentration of the drier is increased, the effect of increasing temperature is less marked. At any given temperature, the effect of the added drier reaches a maximum, beyond which any increase in the amount added will not increase the rate of oxidation.

Mackey and Ingle (348) make several generalizations regarding the nature of prooxygens. These are:

1. A metal, which exists in more than one state of oxidation, acts as a drier if the salts of its lower oxides are more stable than those of its higher oxides.

2. The more oxides which a metal can form, the greater is the catalytic power.

3. Oil-soluble metal salts are strong accelerators of oxidation processes.

From a study of the drying times of linseed oil and various driers, Mackey and Ingle found the following order of effectiveness, starting with the most effective: Co, Mn, Ni, Ce, Pb, Cr, Fe, V, Na, Bi, Ag, Zn, Th, Hg and Al

Evans, Marling and Lower (347) studied the change in certain chemical properties of linseed oil, with added driers. An increase in drier concentration caused an increase in the acid number as well as a decrease in drying time. They conclude that the drier, probably through physical changes, accelerates the slowest of the various chain reactions involved in the oxidation of the oil.

Increased concentration of drier also caused a more rapid decrease in the iodine value. In studying equimolecular amounts of various driers, they found that cobalt, manganese and lead decrease progressively in their activity.

Rouche (349) explains the lethargy of lead driers on the basis that it decomposes the peroxides to monoxides and free oxygen.

Wolff and Zeidler (350) state that the optimum ratio of lead to manganese is 6:1; the optimum concentration of manganese is given as 0.1%.

Currier and Kagarise (351) found that cobalt and manganese linoleates are more active than lead linoleate. Linoleic acid with added drier had a short induction period and absorbed much oxygen whereas oleic acid with added drier had a long induction period and absorbed little oxygen.

Long and McCarter (352) cite data to show that some driers accelerate an oxidation reaction, while others accelerate an association reaction. In the presence of

0.29% cobalt resinate, the gelation time of linseed oil was reduced from 5-3/4 hours to 2 hours, while the oxygen absorption was practically the same as that of the pure oil. Lead resinate also accelerates gelation, but the amount of oxygen absorbed is 18.5 per cent less than for the pure oil. Furthermore, increased temperature seems to accentuate the association reaction of the lead drier, but has very little effect on the oxidation reaction of cobalt drier. Midlam (353) also believes that drier action varies with the particular metals.

Long, Rheineck and Ball (354) state that an increase in the percentage of drier causes an increase in the volume of oxidation products evolved during the early stages of drying.

Weger (355) states that manganese drier increases in action up to 0.2 per cent, and is constant thereafter.

Nicholson and Holley (356), in studying the action of driers in paint films, found that there is a limiting drier concentration above which no appreciable acceleration of drying is obtained. In the cases of cobalt naphthenate and cobalt resinate, the rate of gain in weight depends upon the concentration of the cation, and not upon the anion of the drier material. Titanium dioxide pigment has a retarding effect on the rate of gain in weight of the paint film.

Goldschmidt and Freudenberg (357) found that potassium ferricyanide is a catalyst for the oxidation of oleic acid.

Nakamura (358) studied the oxidation effects on soybean oil. He states that β -naphthol is pröoxygenic in a concentration of 0.05%-0.2%, but above 0.6% concentration, it acts first pröoxygenic and later antioxygenic. Carotene also exhibited a variable effect in catalysis. Hydroquinone, α -naphthol and vanillan do not affect the decomposition temperature of the soybean oil peroxides. Manganese abietate and lead linoleate reduce this temperature from 110° C. to 75° C.; acid clay, kieselguhr and active carbon reduce the temperature to 20°, 30°, and 60° C., respectively.

Wornum (343) states that zinc oxide has a sensitizing and carbon black a stabilizing action on the phase stability of drying oils.

Skellon (359) remarks that blown whale oil is a potent pröoxygen in the blowing of oleic acid at 120° C. It reduces the time of blowing and changes the nature and amounts of products to some extent.

Bradley, Kropa and Johnston (360) found that the oxygen conversion of polyethylene maleates, which are considered analogous to drying oils in this respect, is accelerated by benzoyl peroxide, boron trifluoride, and minute amounts of soluble cobalt and uranium salts.

Morrell and Wood (361) state that silica has no accelerating action, but rather a retarding action due to increased film thicknesses. Lithopone, titanox and leaded zinc retard the rate of oxidation, and decrease the amount of oxygen absorbed, but cause the oil to harden more rapidly. White lead pigment reduces the initial oxidation and behaves later as a drier. Barium sulfate retards the initial rate of oxidation, and decreases the amount of oxygen absorbed; it increases the volatile matter to more than one-half the original weight of oil.

They classify six types of driers as follows: (1) fine metals, (2) oxides, (3) acetates, (4) borates, (5) salts of drying oil acids, and (6) resinates. The only three commercially important elements in this respect are cobalt, manganese and lead. In equal concentrations of 0.05 per cent metal, the activities drop from 100 for cobalt to 46 for manganese, 17 for iron, 13 for copper, and 6.5 for lead. Metals and oxides must be dissolved in the oil by means of heat; the other esters are prepared in spirit solution and can be added directly to cold oils. They consist of soaps prepared by heating together the metallic oxide and the free acid. Resinates are usually rosin acid (abietic acid) esters.

Lead drier is used for film character (i.e. toughness and elasticity); cobalt and manganese driers are used for speed. The latter produce leathery films which have a tendency to crimp. In commercial practice the usual concentrations are: 50 to 150 parts lead per 10,000 parts oil, and 5 to 15 parts cobalt or manganese per 10,000 parts of oil.

III. Antioxygens

In the oxidation and polymerization of drying oils, the behavior of natural antioxygens in the oil and of added materials of a like nature is a very important factor in determining the drying time of oils, paints and varnishes.

There are probably four distinct theories related to the action of antioxidants. These may be classified as follows:

1. Negative catalysts destroy positive catalysts (Luther and Titoff - 1903).

2. Retardation of heterogeneous gas reactions by adsorption of products at a catalytic surface (Langmuir).

3. Substances which retard oxidation by oxygen are themselves capable of being oxidized (Moreau and Dufraisse).

4. Chain reactions in which substances that are able to reduce the average length of the chain, behave as retarders.

Rideal and Taylor (329) consider the action of the inhibitor as a reaction with the autocatalysts or peroxides of the oil molecule.

Smith and Wood (367), from studies on the inhibiting action of 0.25 per cent $SnCl_2$, eugenol, $Na_2S_2O_3$, Na_2SiO_3, and $(CH_2)_6N_4$, respectively, on the oxidation of cottonseed oil at 35° C., conclude that the antioxygens protect the double bonds for a period of time depending upon the temperature, concentration and products of oxidation. Their conclusions may be summed up as follows:

1. The anti-oxygen, being basic, combines with the acidic products of oxidation and prevents them from acting as autocatalysts toward oxidation.

2. The triple bonded nitrogen atom with two partial valences, or elements with free valences, form intermediate compounds with the easily oxidized ethanoid carbon.

3. The temperature controls the rate of reaction for a definite, but limited period of time.

Moureau and Dufraisse (368) have developed the so-called "mutually antagonistic" theory of inhibitor action. The peroxides are destroyed by the interaction of the original active peroxides of the autoxidant, A, and the inhibitor, B, as follows:

$$A + (O_2) \longrightarrow A\ (O_2)$$

$$A\ (O_2) + B \longrightarrow A\ (O) + B\ (O) \longrightarrow A + B + O_2$$

$$B + O_2 \longrightarrow B\ (O_2)$$

$$A\ (O_2) + B\ (O_2) \longrightarrow A + B + 2O_2$$

There are several objections to this theory, viz.:

(1) the disappearance of the energy of activation is not accounted for,

(2) inhibition is not permanent, and

(3) the addition of organic peroxides to autoxidants should liberate oxygen and thereafter act as inhibitors.

Milas (334) states that the kinetics of the reaction require a chain mechanism. The inhibitors must be easily oxidizable; however, anthraquinone, sulfuric acid, $FeCl_3$, $ZnCl_2$ and I_2 inhibit reactions and are not easily oxidizable. Some inhibitors form complexes with the autoxidant, and often they are selective in their action. All inhibitors possess molecular valence electrons and exchange energy with peroxides. This action partially activates the inhibitor molecule, which then is either oxidized or combines with the active autoxidant to form complexes which decompose to the original inhibitor molecules. Milas gives the following expression for the maximum oxygen absorption rate:

$$Vm = K \frac{t}{C^{1/n}}$$

where t = induction period
C = concentration of inhibitor
K and n = constants

When $C = 0$, an explosion will occur unless there are wall effects or similar chain-breaking mechanisms.

Stephens (369) claims that the drying of an oil is essentially a polymerization phenomenon which involves a chain mechanism. In such reactions, inhibitors act by colliding with activated molecules and dissipating their energy of activation. A concentration of 0.1 mol per cent may reduce the average chain length and the reaction rate to 0.1 of their normal values. However, none of the evidence up to now has indicated that the drying of an oil is a chain mechanism; therefore, Stephen's theory has been largely neglected.

In the field of inhibitors, the natural antioxidants present in the raw oil are of primary importance. According to Hilditch (370), these natural antioxygens are non-volatile, active inhibitors of oil oxidation. Most of the evidence for their existence is indirect (e.g. distilled esters), but some direct evidence has been forthcoming. Hilditch states that fresh cod liver oil resists oxidation at moderate temperatures for many hours, but finally absorbs oxygen and develops a peculiar, sharp smell. Furthermore, the decline in vitamin A potency parallels the oil's power of resistance to oxidation. Ivanow and Eyre established that the most highly unsaturated components of the oil are produced in the later stages of the ripening of the seed - i.e., at a time when the molecule is particularly freely exposed to the air - yet the oil extracted from ripe seed normally contains no oxidized glycerides.

In a later article, Hilditch and Sleightholme (362) found that the induction period of olive oil was almost eliminated if treated with caustic soda or dilute hydrochloric acid, but the induction period increases if the oil is warmed with 1 per cent concentrated H_2SO_4. They conclude that the antioxygens are water-soluble and easily hydrolyzed; the results with H_2SO_4 suggest addition to the double bonds and consequent strong antioxidative action.

The term "inhibitols" has been suggested by Olcott and Matill (371) for the natural antioxygens of fatty oils. The "ol" indicates the presence of a hydroxyl group. They found that inhibitols were always inactivated by reagents which combine with the hydroxyl group.

Royce found that gossypol ($C_{30}H_{30}O_8$), a polyhydroxy phenolic compound which occurs in cottonseed, greatly increases the induction period of cottonseed oil. As little as 0.2 per cent increases the time threefold.

Holm, Greenbank and Deipher (372) likewise consider gossypol the active antioxygen of crude cottonseed oil.

Matill and Crawford (373) found that refined maize oil had a reduced induction period. Originally, they thought the change was due to the removal of sterols. Later they found that purified cholesterol and sitosterol are not antioxygenic; they suggest that vitamin activity is probably more significant.

Greenbank and Holm (374) studied the natural pigments in oils; they found that carotene was pröoxygenic, lycopene neutral, and quercetin antioxygenic. This agrees with the results of Franke (375), who showed that lipochromes accelerate the oxidation of glycerides; however, Monahan (376) and Newton (377) class carotene as an antioxidant.

Cohen (378) isolated cephalin from the aqueous extract of fresh linseed oil. This and chlorophyll and xanthophyll inhibit oxidation in the dark. He concludes that the natural antioxidants are probably phosphatides, chlorophylls and carotenoids.

Long and Wentz (379) confirm this viewpoint by showing that small percentages of mucilaginous matter and phosphatides exert a decided influence on the bodying rate of linseed oil.

The effects of artificially introduced antioxygens have been studied by numerous investigators. Probably the earliest of these was Chevreul, who showed that oak wood, poplar wood and pine wood retard the drying of linseed oil. Moureau and Dufraisse (368) attribute this to the antioxygen action of tannin in the wood bark.

Moureau and Dufraisse (loc. cit.) also found that phenols prevent the transformation of acrolein into disacryl; naphthol, hydroquinone and pyrogallol also exhibited this antioxigenic activity. Thiophenol was found to exhibit a reversal of action on the oxidation of linseed oil, being first prooxygenic, and later antioxygenic. The antioxidative characteristics of phenolic compounds in the oxidation of oils is also shown by Matill (380), Tanaka (381), Banks (382), Greenbank (374), Yamaguchi (383), Wagner (384), Rogers (385), de Conno (386), and Nakamura (387).

Matill (loc. cit.) found that meta phenols are inactive, whereas ortho and para types are effective. Side chain phenolic groups are likewise inactive.

Yamaguchi (loc. cit.) found that 0.1 per cent hydroquinone inhibited the oxidation of triolein. When copper oleate and hydroquinone were added to oleic acid, the former inhibited the antioxygenic action of the latter, and itself acted as an antioxidant. Copper oleate acts as a procatalyst for the oxidation of hydroquinone, and therefore inhibits the natural tendencies of the latter.

Wagner and Brier (loc. cit.) worked to try to arrest the oxidation reaction when the linseed film possessed its most desirable properties. They used hydroquinone as the antioxygen. They first started by exposing linseed-hydroquinone films to air; however, the anti-oxygen prolonged the induction period as long as a year, and too many errors were introduced to obtain accurate results. Then they used a less popular method; i.e. blowing the oil and running iodine numbers on the blown oil. They discovered that hydroquinone had no appreciable antioxygen powers in concentrations less than one part in 10,000. Additional portions of hydroquinone after the oxidation had started, showed that the additions were effective if they were not made too close together. They also found that the addition of 25 per cent of oxidized linseed to 75 per cent raw linseed, containing an effective amount of hydroquinone, shortened the induction period considerably. They concluded that the velocity of the oxidation reaction determines the effectiveness of hydroquinone as an antioxygen.

Rogers and Taylor (loc. cit.) obtained oxygen absorption-time curves to show the inhibiting action of hydroquinone, β -naphthol, diphenyl amine and combinations of cobalt drier and diphenylamine. Although 1 per cent of the latter was a strong inhibitor, an addition of 0.003 per cent cobalt drier nullified this action and produced an accelerated oxidation. Other results show that the inhibitor action is not greatly affected by temperature, but that the inhibitor is slightly more effective at low temperatures.

De Conno, Goffredi and Dragoni found that phenolic compounds did not check the oxidation of linseed oil which had previously been blown 24 hours at room temperature. However, acetic and glycollic acids were effective retarders. Taradoire found that aromatic amines are more powerful antioxidants than phenols.

Nakamura (loc. cit.) states that β-naphthol is prooxygenic towards soybean oil at a concentration of

0.05%-0.2% inhibitor, but that the reverse effect occurs at concentrations above 0.6%.

Greenbank and Holm (loc. cit.) found that only ortho and para phenols are active antioxidants for oils; they tested the activity of hydroquinone, catechol, resorcinol, hydroxyhydroquinone, pyrogallol and phloroglusinol. In the order named the protective factors (millimoles of peroxide per kilogram of untreated fat/ millimoles of peroxide per kilogram of treated fat) are as follows: 3.7, 2.0, 1.1, 3.6, 3.6, and 1.0. They also showed that maleic acid, which has a structure very similar to hydroquinone, is an effective antioxidant, but its stereoisomer, fumaric acid, is worthless in this respect.

Vernon and Rinne (388) studied the antioxidant influence of phenol-formaldehyde resins on unbodied linseed oil in the presence of driers. The six phenol-formaldehyde resins and mixtures of these resins with ester gum, showed marked antioxygenic effects in direct proportion to the amount of resin present. This effect was specific for each individual resin, and was confined to the induction period. This antioxidant effect was partially due, in two cases, to some oxidizable part or component of the resin, since it was markedly decreased when the resin was treated with oxidizing agents. This last fact was in accord with the theory of Moureau and Dufraisse (368) relative to antioxygens, and indicated a possible treatment of such resins should their antioxygenic properties be undesirable.

The resins studied were apparently free from simple phenols used in their manufacture, although one of the resin-ester gum mixtures yielded a considerable amount of a complex phenol. The presence of free formaldehyde could not be demonstrated; yet in one case a behavior was noted which indicated the possibility of its presence.

Olcott and Matill (371) prepared the crude methyl and ethyl esters of cottonseed oil acids. The oxygen absorption was strongly inhibited by aliphatic dibasic acids, H_2SO_4, H_3PO_4, phenolics and inhibitols (concentrated unsaponifiable matter from the oil).

Robinson (389) nullified the prŏoxygenic activity of haemoglobin, methaemoglobin and haemin in linseed oil by adding excessive amounts of potassium cyanide.

Long and Egge (390) found that 0.5 per cent α-naphthol prevented the oxidation of linseed oil at 30° C. for 100 hours even in the presence of 0.1 per cent manganese. They also found that thioglycollic acid, by precipitating metallic driers, effectively inhibited the further oxidation of the oil.

IV. Light Radiation

The procatalytic effect of ultraviolet light radiation has been observed by many investigators. Milas (334) found that irradiated distilled water liberated iodine from starch-iodide solution, due to the formation of peroxides.

Elm (391) states that linseed oil drying is accelerated by light only if the radiation is partially absorbed. The degree of unsaturation or the field of residual valency determines the selectivity and degree of absorption. If the absorption is strong in the visible rays, color will result. Polymerization causes a displacement of the absorption to shorter wavelengths, and decreases the depth of color.

Horio (392) found that the rates of oxidation of linseed oil, olive oil and linoleic acid, when irradiated with a mercury quartz arc, were directly proportional to the square root of the light intensity. Horio and Yamashita (393) found negligible changes in acid value, iodine value and refractive index immediately after exposure to the mercury lamp. However, when later blown, these oils changed properties much more rapidly than untreated oils. The light is stated to activate the oil molecule and initiate a chain reaction like the following:

$$A\ (\text{oil}) + h\nu \longrightarrow A'$$

$$A' + O_2 \longrightarrow AO_2'$$

$$AO_2' + A \longrightarrow A' + AO_2$$

$$AO_2' + M\ (\text{Solvent}) \longrightarrow AO_2 + M'$$

$$M' + A \longrightarrow A' + M$$

Similar observations of enhanced activity from light irradiation have been made by Taüfel (394), Nakamura (387), Scheiber (395), Lewkowitsch (396), and Nicholson (397).

Gardner (398) used this principle in designing an apparatus, consisting of a revolving metal drum and a low pressure Hg-quartz tube, for the rapid oxidation and polymerization of oils.

V. Electric Impulses

Long and McCarter (352) state that polymerization is accelerated by electrical energy. The absorption of this energy can be greatly accelerated by the presence of intermediate sensitizers, such as halogens.

VI. Cathodic Rays

Long and Moore (399) studied the action of cathode rays on perilla oil, linseed oil and chinawood oil. Tests on perilla show an overall decrease in hexabromide number corresponding to a change of 0.061 g. of linolenic acid to the insoluble isomeric form per gram of oil. Calculations from the iodine number indicate that two double bonds are closed in the process. The refractive index increases in linseed and perilla oils, but decreases in tung oil; the molecular weight increases steadily in all cases.

Kittelberger (400), in studying the action of cathode rays on linseed oil, shows that the iodine value decreases, the refractive index increases, and the acid number slightly increases. Similar but smaller changes occur in an atmosphere of nitrogen. Overexposure chars the oils, but short exposures in air cause a bleaching action. Raw linseed which has been rayed dries in a few hours.

He suggests that the rays act by destroying the natural oil inhibitors, but other reactions are also occurring. Evidence is shown that an isomeric change is produced in the oil.

VII. Inorganic Catalysts

The action of ozone on oleic acid and linseed oil has been studied by Briner and his associates (401). They obtained negative results in their attempts to show that ozone is the active catalyst in normal autoxidation. However, the use of less than 0.5 per cent ozone in air or oxygen caused the oil to dry in one-half the normal time. Higher concentrations than this retard the final stages of drying and produce an opaque, brittle film.

Marcusson (402) found that 5 per cent $SnCl_4$ in CS_2 solution, polymerized tung oil at room temperature. Larger concentrations (50%) polymerized linseed oil at the temperature of the water bath.

Beatty (403) observed that $FeCl_3$ or $SnCl_4$ cause the rapid gelation of blown linseed oil. These gels are more plastic and cohesive than those of tung oil.

Chowdhury (404) found that oleic acid formed highly viscous polymers in the presence of $SnCl_4$. The heat evolved suggests the formation of unstable, intermediate complexes, which subsequently break down, activate the acid molecule, and cause polymerization.

Long and McCarter (352) state that metallic chlorides, especially those of iron, tin and aluminum, catalyze the polymerization of oils at room temperature.

Whitby and Chataway produced gelation of drying oils with sulfur instead of oxygen. They also cite the catalytic effects of $FeCl_3$ and $SnCl_4$ in the polymerization of tung oil.

VIII. Acids and Bases

The accelerating effect of free fatty acids during the oxidation of fatty oils is well known. Long and Chataway (405) found that a mixture of 15 per cent fatty acids and 85 per cent glycerides gelled much faster and absorbed less oxygen than the oil itself.

Long and McCarter (352) observed similar results in their study of the effect of acid value on the blowing of linseed oil.

Wornum (343) states that fatty acids are ready dispersing agents for oil micelles. In this capacity they should partially stabilize the micelles, and thus control the ultimate particle size in the gelled oil. The acids, being polar, probably orient at the active micelle spots and prevent further cross-linking. Too great an addition of acids will prevent gelation and impair the drying properties of the oil.

Rona and his associates (406) found that pyridine and nicotine increase the oxidation velocity of methyl linoleate, proportional to their concentration and to the pH of the solution. Acids have similar effects.

Franke (375) states that linoleic acid oxidizes more rapidly in basic than in neutral solvents; aniline in ethyl alcohol exerts a catalytic effect. Other substances in the order of increasing effectiveness, are: urea, KOH, Et_2NH, NH_3, lecithin, and $C_2H_4(NH_2)_2$. The oxidation of oleic acid is catalyzed by pyridene, piperidine, Et_2NH, and proline, but is inhibited by aniline and dimethyl aminobenzene. The oxidation of linoleic acid is catalyzed by glyceraldehyde, $CO(CH_2OH)_2$ and acetaldehyde. Cholic acids and cholesterol have little or no effect; however, egosterol is an active catalyst.

PRESSURE EFFECTS

I. General

The applications of pressure to the facilitation of chemical processes has attained importance only since about 1913. The advantages of high pressures lie in the fact that many systems which undergo no change at atmospheric pressure will react to give practical yields if the pressure is increased to a few hundred atmospheres. According to Morgan (444) the advantages of pressure are twofold: (1) It diminishes the volatility of reagents; retains them in the liquid phase even at temperatures above their atmospheric boiling points; and (2) it increases the concentration of gaseous reagents and facilitates their reaction, particularly if said reaction is accompanied by a decrease in volume.

The first of these advantages occurs in the reactions of volatile liquids, such as (1) the hydrolysis of fats and oils with water, using 3 per cent base as catalyst and conditions of 170°C. and 8 atm. pressure, (2) alkylation of aromatic amines (e.g. aniline and methyl alcohol at 230°C. and 30-40 atm. in the presence of H_2SO_4), and (3) the interconversion of naphthols and naphthylamines.

The second advantageous use arises in processes such as (1) the Haber process, (2) methanol synthesis from CO and H_2 at 200 atm. and 420°C. using zinc chromite catalyst. By varying the conditions and the catalyst, higher alcohols, acids and aldehydes are possible.

Frolich (445) discusses the use of pressure in various processes and stresses its effect on the equilibrium and the rate of reaction. He suggests future applications in the preparation of acids from alcohols and CO, the oxidation of paraffins, and the syntheses of proteins from ammonia and fatty acids, and that of sugars from aldehydes.

Other excellent reference works of a general nature are those of Groggins (442), Ipatieff (441), Perry (443), Brown (446), Bridgeman (447) and engineering journals (448).

II. Heterogeneous Reactions

Morgan (444) mentions the Bergius process for the hydrogenation of coal. Powdered coal is treated with hydrogen at 470°C. and 200 atm. in the presence of tar and hydrated ferric oxide. A viscous oil containing mostly aromatic hydrocarbons is produced.

A review of liquid phase reactions is given by Fawcett and Gibson (449).

III. Oxidation

Morgan (loc. cit.) and Groggins (loc. cit.) mention the use of pressure in oxidation reactions. Morgan points out the conversion of pyridine to α, α'-dipyridyl at 350°C. and 50 atm. using anhydrous $FeCl_3$ as a catalyst.

IV. Polymerization

Morgan (loc. cit.) also states that pressure has a strong effect on the polymerization of olefins such as ethylene; boron trifluoride is recommended as a good selective catalyst. Bridgman and Conant (450) found that amylene and other olefins were unaffected by pressures as high as 12,000 atmospheres at room temperature; however, indene, isoprene, styrene and the like readily polymerized.

Starkeweather (451) states that unsaturated organic compounds with conjugated double bond systems polymerize at 2000-9000 atmospheres and at 20-74°C. Chinawood oil likewise polymerizes but castor oil does not.

Long and McCarter (452) state that drying oils will polymerize at room temperature under the influence of very high pressures.

Frolich (445) claims that amorphous solids will polymerize under pressure.

Conant and his co-workers (453,454) review the high pressure reactions of polymerization including the mechanisms involved.

V. Design and Operation

In the design of high pressure equipments, several special factors must be considered. Perry (443) gives in detail the variables involved in the selection of materials and the design of apparatus. Joints must be made pressure-tight either by threads, metallic bonds or mechanical compression with line contact or with gaskets. In tightening a closure against a gasket, the various bolts must be gradually tightened at every point. Valves for high pressure work differ only in the thickness of walls and in the high pressure drop across the seat which makes gate valves impractical and causes severe erosion in regulating valves. Sight glasses and electric leads should be provided. Reaction vessels are usually forged cylinders, although welded equipment is becoming more popular. For further details on this subject refer to Perry (loc. cit.) and Catalog 406 of the American Instrument Company, which discusses also the accessory equipment for experimental autoclaves. Pumps, compressors and gas storage chambers must be provided.

For the measurement and control of pressure reactions, the investigator can have recourse to Bourdon tubes, dead weight gages, thermocouples, flow meters and level indicators. The accuracy and sensitivity of these instruments is essential for determining the state and the homogeneity of the reaction mass at any one moment. In the development of a commercial process, these are the only means of standardizing the conditions of operation. Keyes (455) gives an excellent discussion of the apparatus for measurements of temperature, pressure, and volume. Blücher (456) and Kleinschmidt (457) discuss the technique involved in high pressure work.

The safety of the worker is of foremost importance in high pressure work. For that reason, I have quoted from Perry (loc. cit.) the following essential precautions:

> "(1) To permit the escape of gases the cases of Bourdon gages should be bored with a large number of holes, or should be provided with large openings lightly covered with lids held in place by springs. Whenever possible, the gage glass should be removed and the face left open or the glass replaced with thin transparent sheeting or with safety glass so that the effect of flying particles will be minimized. The usual procedures should be followed, such as the use of oil seals to prevent corrosion, throttling down to prevent fatigue, and the use of built-in checks to prevent the pressure from rising or falling too suddenly.
>
> (2) With inflammable gases at high pressures, the Armstrong effect is a possible source of trouble: when a gas containing finely divided liquid or solid particles passes at high velocity over an insulated metallic object, that object becomes electrically charged. The charge may become sufficiently great to cause a spark, which in turn ignites the gas.
>
> (3) Where it is not possible to use a self-seating safety valve, it is sometimes possible to have two safety valves: one set slightly above the operating pressure with a shut-off valve between it and the body to be protected, and the other set somewhat higher and without the shut-off valve.
>
> (4) A variety of pressure relief that has met with favor because of its positive action and because it cannot readily be prevented from

blowing off when the pressure exceeds a certain value, is the rupture disk, which consists of a plate held in place over an opening by means of flanges in such a way that it is subject to simple shear. When the pressure rises too high, the disk ruptures. The disadvantages of the method are that the entire contents of the pressure system are discharged, and that corrosion may so weaken the disk that unless frequently inspected and renewed it may burst at too low a pressure; on the other hand, since the working pressure produces stresses close to the yielding stress of the material of the disks, they tend to become strain hardened with continued use and may then fail to relieve the pressure at the desired point.

(5) Some catalysts, notably very active nickel or iron powders, are highly pyrophoric. Where there might be a danger of their leaking through valves or stuffing-boxes, drying out and glowing, it is desirable to provide a constant stream of water to wash them away so that any inflammable vapors or gases that accompany them may not catch fire.

(6) The larger and hotter pieces of high-pressure equipment may be placed to advantage behind heavy barricades, for in case of failure, heavy walls and light roofs give protection to the surroundings. At the same time it should be urged that anything permitting the formation of gas pockets is to be avoided.

(7) Since leaks are a serious fire or health hazard, they should be repaired as promptly as possible, especially as erosion quickly makes the leak worse and may cut into the metal so severely as to require replacement of a portion of the apparatus. Leaks should never be tightened under pressure.

(8) Oxygen cannot be compressed with safety in the presence of oil (Hersey, A Study Of The Oxygen-Oil Explosion Hazard, J. Am. Soc. Naval Eng., 36, 231 (1924)), so that water must be used as a lubricant. It has been found that when oxygen is admitted rapidly at high

pressures into a space containing a bit of oily material explosions may ensue. Every reason indicates that pressure should always be built up slowly.

(9) The periodic inspection of high-pressure equipment is a very real necessity and is a matter of routine in all high-pressure plants."

VOLATILE PRODUCTS

I. Oxidation Of Oils

The evolution of volatile constituents of varied composition during the drying of a fatty oil has been observed by numerous investigators in a qualitative manner. Their results have been summarized for ready reference on the following page.

Milas (408) postulates the possible formation of hydrogen from -hydroxy alkyl peroxides, in the following manner:

$$\mathrm{ROOCHOHR'} \xrightarrow{\text{(alkalis)}} \mathrm{H} + [\mathrm{RO-}] + \mathrm{R'COOH}$$

$$2[\mathrm{RO-}] \longrightarrow \mathrm{R{-}OH} + \mathrm{R''CHO}$$

Wislicenus (421) offers a unique explanation for the formation of formic acid. He considers this a product of the reduction of CO_2 by hydrogen peroxide.

A few investigators have attempted quantitative measurements of the various constituents in the volatile products. In all cases the actual quantities were very small, so that accurate measurements were difficult.

Skellon (411), in the uncatalyzed oxidation of oleic acid, found traces of formic acid, acetic acid, CO_2 and H_2O in the volatile products; the carbon loss, as determined by ultimate analysis, was very much less than one atom per oil molecule. In the catalyzed oxidation of oleic acid, he detected CO_2, H_2O and traces of formic acid, acetic

TABLE B

VOLATILE PRODUCTS IN THE OXIDATION OF OILS

				FATTY ACIDS									ALDEHYDES								
Reference Number	H_2O	CO_2	CO	Formic	Acetic	Propionic	Butyric	Oxalic	Peracids	General	Esters	Peroxides	General	Acetaldehyde	Acrolein	Unsaturates	Hydrogen	Oxygen	Alcohols	Hydrocarbons	Methane
407	D	D	D									D	D								
408									D								D				
409										D		D	D						D		
410										D		D	D						D		
411	D	D	D	D	D			D						D							
412		D	D													D	D			D	D
413		D																		D	
414										D			D		D						
415	D									D										D	
416		D								D		D									
417	D	D		D	D					D											
418							D														
419							D														
420			D																		
421				D																	
422	D	D	D							D			D								
423										D			D								
424		D															D	D		D	
426	D	D								D			D								
427															D						
429										D	D		D						D		
430													D			D					
431															D						
432	D	D													D						
433		D	D	D						D			D								
434	D	D				D		D		D									D		
435	D	D								D			D								
436	D	D								D											
437	D	D								D	D		D								

* D = detected in traces or more

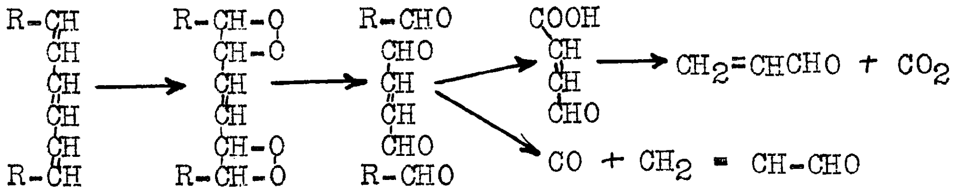
acid, oxalic acid and acetaldehyde; the carbon and hydrogen loss was three per cent and the amount of volatile products was 1-2 per cent of the original acid.

Newington (412) used an absorption train, including I_2O_5 absorbers, to detect the presence of carbon monoxide produced from painted surfaces in ship storerooms. Hydrocarbons, H_2 and unsaturates were also detected. A five months old sample of boiled linseed evolved over 3 per cent CO_2, 0.35 per cent CO and amounts of hydrogen and hydrocarbons below 0.05 per cent.

Coffey (416) oxidized linseed oil at 100°C. and found that the CO_2/COOH ratio was 1:1 for the oil. He states that the acidic products come from the linolenic acid; one CO_2 is also produced for each molecule of acid. Morrell (438) agrees that the linolenic acid content of the oil is responsible for the volatile acidic products.

Lyntenberg (423) determined 0.37 per cent acids and 0.62 per cent aldehydes on the weight of the oil.

Salway (427) detected acrolein qualitatively by means of bromine water and odor, and quantitatively by precipitation of the silver salt. He found that the oil liberates 0.37 grams of silver acrylate per 100 grams of oil. The following mechanism is suggested:



Long and McCarter (434) used an absorption system and ultimate analyses to determine that acids, aldehydes, alcohols, CO_2 and water are formed and that the atomic ratio of hydrogen to carbon in the volatile products varies from 3.5 to 10.5 depending on the temperature (inversely) and the presence of acids and driers. The amount of volatile products varied from 3.5-5 per cent of the original oil.

Long, Rheineck and Ball (435) found that oxidation at 7°C. produced 0.14 per cent H_2O, 0.045 per cent CO_2, and 0.065 per cent acids, whereas at 52°C., there was produced 0.80 per cent H_2O, 0.025 per cent CO_2, and 0.062 per cent acids. Driers and pigments tended to somewhat increase these amounts. They used an absorption system of calcium chloride, ether, ether + water, and potassium hydroxide solution.

Wacholtz (437) carefully studied the evolution of CO_2, H_2O and acids during the blowing of linseed oil. He used an air washing unit, a reaction unit, an absorption unit and a pumping unit. The air was carefully washed, dried and decarbonated. The gases were absorbed in calcium chloride, ether + ethyl alcohol, and weak caustic potash solution. He determined the following results: 3.61 per cent H_2O, 1.93 per cent acid, and 2.92 per cent CO_2, based on the initial weight of the oil.

II. Heat Bodying Of Oils

Cutter (439) states that water and low molecular weight acids and aldehydes are produced during the heating of an oil.

Van Horne (440) examined the gases of the decomposition of linseed oil heated to its critical temperature in a closed vessel. The evolved gases caused a red-brown coloration in the oil. When a single phase was obtained, he considered the temperature as the critical temperature. The gas was transferred to a test tube and analyzed by pressure methods; the gasses amounted to 18 per cent of the original oil. After being washed in one per cent H_2SO_4, the gases were passed successively through pipettes containing KOH, bromine water, pyrogallol and cuprous chloride; the residual gas was burned in a combustion pipette and the results calculated to hydrogen, ethane and nitrogen. The results follow:

(1) KOH removes 20.6%, probably CO_2 and acids
(2) Bromine water removes 2.9%, probably unsaturates
(3) Pyrogallol removes 2.9%, probably oxygen
(4) Cuprous chloride removes 16.2%, probably CO
(5) Combustion calculations yield: 44.2% C_2H_6, 9.9% H_2 and 3.9% N_2

The combustion of the gas, remaining after absorption, caused a large decrease in volume, a slightly smaller quantity of CO_2 produced, a very large amount of oxygen consumed, and residual gas which defied combustion.

III. Heating Of Oxidized Oils

When oxidized oil films are heated, water, CO_2 and a loss in weight are found, according to the experiments of Long, Rheineck and Ball (435).

#100 OIL

At Lehigh University, the production and study of the properties of completely blown linseed oil, designated "#100 oil", was carried on for several years under the direction of Dr. Long. The preliminary work and results are the product of many assistants, but most of the work was done by Wacholtz (461), Lutz (462), Chapin (463), Beal (464) and Taylor (465). This gelled oil-product was of particular interest because of its solubility in the ordinary lacquer solvents such as acetone, ethyl alcohol and higher alcohols-amyl, butyl and cyclohexanol. Ordinary linseed oil is incompatible in these solvents and can only be used in short oil lacquers. This new product can be used in long oil lacquers to which it gives unusual flexibility.

I. Production

The general blowing procedure is as follows: a gallon of drying oil is placed in a two gallon glass vessel resembling a tall, inverted bell jar. The bottom of the vessel is fitted with a fritted-glass air distributor, which in turn is fitted to a source of cleansed air under pressure. The oil may be heated by immersing an ordinary electric light bulb in the oil. The blowing operation commences as soon as the air is turned on and continues until the desired end point is reached. The fritted-glass air distributor disperses the air into fine bubbles which rise through the oil. The blowing should be rather vigorous, so that the oil is mixed as well as processed by the air. The air should be passed through a filter of cotton waste or glass wool to remove all extraneous matter. Removal of moisture or carbon dioxide from the air is not necessary for the usual blowing operation.

The top of the glass vessel should be covered with a lid to prevent splashing and undue loss of oil. This is important since it is very easy to clutter up a laboratory with bits of partially blown oil. In the event that the drying oil being blown has a marked tendency to foam, it will soon foam past the lid and continue to do so until all the oil has been lost. The best example of this is obtained in the processing of raw linseed oil. A motor driven disperser will successfully beat down the ever-advancing foam level. The disperser is a piece of glass rod bent into the form of a stirrer with a working radius of about three inches. It is driven at considerable speed and its action is to throw the fine foam bubbles against the wall of the vessel where they burst and run as a liquid back to the main body of the oil..

The electric light bulb used for heating should be well immersed in the oil and usually a 50 or 75 watt bulb (e.g. Mazda lamp) will heat a gallon batch of oil to approximately 50-50°C. Care must be taken that the oil does not "burn" on the bulb. "Burning" can be detected by the formation of a solid, orange gel on the surface of the light bulb.

After blowing has been started the oil undergoes little or no change for the first twenty hours. When blowing at 50°C. the first change in the appearance of the oil occurs after about 40 hours, the oil darkening slightly in color. Then as the blowing continues, the oil begins to bleach to a light yellow color. This is called the "bleach point" and really consists of a period of 12 hours. A purified brand of linseed oil will bleach after 70 hours of blowing at 50°C. As the blowing is continued, the oil changes considerably in viscosity, but not in color. The viscosity begins to increase perceptibly after the eightieth hour. The air, however, still gives a good mixing action until after 160 hours when the oil has bodied up to such an extent that local heating around the bulb is noticed. The oil distant from the bulb will receive under these conditions no heat due to poor mixing and low heat transfer.

In order to prevent burning of the now semi-gelled oil, the light bulb is removed from the vessel. The blowing progresses. The color remains practically constant while the consistency or viscosity increases. The air finally has to force its way through the oil with difficulty and only large bubbles are formed. Finally after the 250 hour mark is passed the air barely forces its way through the oil. Long elliptical bubbles slowly diffuse through the mass. After about 475-500 hours, the air can no longer force its way through the oil. Then the blowing is stopped and the oil is said to be "blown".

During the earlier part of the blowing operation, that is, after about 60-70 hours during the bleaching period, the reaction with the air becomes noticeably exothermic, especially in the case of raw linseed oil. In this case the oil may actually "burn" in the sense that it turns into a dark black-brown insoluble gel, approaching the consistency of a resinous gum. This exothermic reaction is characteristic for most drying oils and should be taken into consideration in choosing the blowing temperature, size of container, etc. As already stated, the blowing process continues in most cases peacefully after this "bleaching" period is passed. There is a steady increase in the viscosity of the oil until a point is reached where the air can no longer force its way through the mass.

II. Properties

Starting with a high grade of refine linseed oil the resulting product should be a homogeneous, light yellow, strong, sticky, oil gel. It has a specific gravity of approximately 1.000. It can be removed from the container best by pulling it out by the hands much like "taffy pulling". Upon removal it should be immediately stored in air tight containers replacing the remaining air in the container with an inert gas. Carbon dioxide has been found suitable for this purpose. If the oil is to be stored for use in lacquer formulating, it can be dissolved with alcohol and may, in this way, be kept in liquid form without risking further oxidation.

According to Wacholtz, the following procedure should be used in dissolving the gel:

> "-50 grams of oil gel weighed into a 150 cc beaker are heated slowly upon an electric hot plate until the gel melts. This will occur at a temperature of approximately 90°C. Care must be taken not to over heat the gel, lest it becomes completely useless. When the gel is completely molten, it should be a light yellow, oily liquid and ready to be diluted with alcohol. Thirty-three grams of ethyl alcohol (95 percent pure) are then added slowly to the molten oil. The alcohol must be added so slowly that it will not chill the oil to the solid condition for then it will refuse to dissolve readily in the alcohol. After the first 10 grams of alcohol have been added the oil should be quite liquid and able to receive the remainder of the alcohol without gelling or precipitation. After the alcohol has been completely added, the solution should be set aside to cool. When it has been cooled to room temperature the solution of oil in alcohol should be a light yellow clear liquid solution. Any lumps of gel or "skins" are regarded as insoluble matter."

The gelled oil has several disadvantages: (1) It oxidizes to a certain extent after it is flowed, (2) during the early stages of drying, the film is soft and tacky, (3) the oil is not miscible, and (4) an exposed oil forms a skin, which refuses to melt or dissolve in any solvents; overheating produces a similar phenomenon.

During the blowing of a drying oil, the viscosity, oxygen content, iodine value, acid number and other variables undergo characteristic changes. Typical results for the first three variables are shown in Table C, which is from the work of Lutz (loc. cit.).

Wacholtz (loc. cit.) has studied the changes in acid number, weight, volatile products and refractive index. The acid number of the oil increases more or less gradually after an initial induction period; in one run the increase was from 1.95 to 9.06. At the same time the oil is gaining weight rapidly and losing water, carbon dioxide and volatile acids. His results on these variables are shown in Table D. The refractive index is also shown to increase during the blowing period; however, he did not follow this variable to the reaction endpoint.

Chapin (loc. cit.) studied the variables of density and surface tension. The density remains constant until the bleach point, and then rapidly increases. The surface tension, however, only remains constant for

TABLE C

Time of Blowing (Hrs.)	Viscosity		Iodine No.	%Oxygen U. A. #	Temp. of Blowing
	Secs.	Gardner-Holt			
0	1.2	A	168.0	10.7	
4	1.2	A	165.9		
20	1.2	A	163.8		
28	1.2	A	162.8		
44	1.2	A	162.5		
53	1.2	A	162.2	11.0	
68	1.2	A	162.2		39.0°C
77	1.2	A	162.2		39.5
92	1.2	A	162.2		39.5
103	1.4	A-B	162.2		37.0
121	1.4	A-B	161.7	12.98	39.0
140	1.4	A-B	159.0		37.0
149	1.6	B-	153.9		38.0
164	1.8	B	142.2		37.0
173	2.0	C	140.4		39.0
188	2.4	D	136.4		39.0
196	3.4	F	127.2		40.0
212	5.0	K	116.6		41.0
222	6.0	Q	112.7		42.5
236	10.0	T-U	110.2		43.0
244	13.4		108.6	17.28	44.0
260	38.0		104.3		46.0
273	53.0		100.0		45.5
300	120.0		95.7		45.5
308	305.0		92.9		46.0
317	715.0		92.5		46.0
332			92.2		54.0
336			92.2	18.95	54.0

U.A. - Ultimate Analysis

TABLE D

Time of Blowing in Hrs.	% Total Gain in Weight	% Total Weight Water Abs.	% Total Weight Acid Abs.	% Total Weight CO_2 Abs.
0.0	----	----	----	-----
8.5	----	0.08	----	-----
20.0	----	0.21	----	-----
27.0	----	0.36	----	-----
42.0	----	0.54	0.01	0.268
63.0	0.10	1.15	0.03	0.485
70.5	0.24	1.34	0.04	-----
91.5	1.34	1.62	0.12	0.533
108.5	2.27	1.97	0.24	0.570
114.0	2.47	2.06	0.28	0.922
135.0	3.15	2.35	0.47	1.109
153.0	3.67	2.57	0.68	1.284
159.5	3.91	2.62	0.79	2.106
167.0	4.48	2.70	0.94	2.439
192.0	4.94	2.77	1.18	2.626
211.0	5.14	2.85	1.31	2.699
235.0	5.37	3.03	1.50	2.771
260.0	5.61	3.14	1.64	2.808
284.5	5.99	3.29	1.70	2.861
306.5	6.46	3.42	1.94	2.916
331.5	6.59	3.53	----	-----
362.0	6.62	3.61	1.93	-----

All weights are based on 100 gms. Oil in the original sample.

three hours. After that it decreases to a minimum in ten hours, and then increases again. This is thought due to the polarity changes taking place in the oil.

Beall, Cooper and Napravnik (loc. cit.) studied the effect of driers during the blowing process. By adding 0.3 per cent Pb and 0.05 per cent Co as naphthenates, they obtained greatly decreased blowing times and found that the oil was less oxidized at the gelation point. By determining the amounts of oxygen in peroxide, carbonyl and hydroxy groups and comparing this with the total oxygen indicated by the ultimate analyses, they found that driers increased the oxygen present in some other form than the tested ones. The solubility of the gel was an inverse function of the drier concentration.

Taylor (loc. cit.) studied the effect of driers on the film formation from #100 oil solutions. These results indicate that driers have but little effect because the oil is well past the induction period. By varying humidity and temperature, he found that: (1) Increased humidity greatly increases the time of blowing but produces a lighter oil gel, which readily melted and dissolved, and (2) increased temperature greatly decreased the time of blowing

Taylor also studied the ternary system: #100 oil - free fatty acids - linseed oil. The free acids acted as a common solvent for the raw and blown oils; a mixture of 10 per cent free acids, 30 per cent linseed oil and 60 per cent #100 oil was miscible and formed satisfactory films in spite of the free fatty acids which were present.

III. Theory

The theories concerning the mechanism of blowing of drying oils have been discussed in detail in the section on the oxidation of oils. The same considerations apply in the production of #100 oil and no further discussion seems necessary.

#101 OIL

One very interesting special product arose from the various studies on #100 oil. Taylor (loc. cit.) in the course of reacting maleic anhydride with blown oils to prove the presence of conjugated double bond systems, obtained a commercially useful product, which he has designated as "101 oil". A brief summary of its production, properties and uses follows:

1. Reaction. Partially oxidized oil (cold blown, preferably) containing from 14 to 17 per cent oxygen (iodine number 130-100) is heated to 50°C. To this is added five per cent by weight of maleic anhydride, and then the temperature is raised and the mixture stirred. At 57-60° C. the maleic anhydride melts, and it goes into solution in the oil. As the temperature is raised a slight foaming occurs. At 90°C. the heating is stopped, and the reaction, which is strongly exothermic is allowed to proceed. A temperature of from 90-100°C. will be maintained by the heat of the reaction, and will continue for 15-20 minutes. The temperature must not be allowed to exceed 110°C., or the reaction will go too fast, and the oil will be gelled and badly charred by the heat. Oils containing about 17 per cent oxygen are best treated in some inert solvent, such as xylol, heating to 100°C., with the anhydride, for one hour being sufficient to effect reaction.

2. Treatment of the Product. When the oil has cooled to 75-80°C., solvents can be added, the oil being readily soluble. The best solvent mixture for the oil was found to be 15 per cent toluol plus 5 per cent ethanol. This gives a stable solution. Additions of from 0.03 to 0.05 per cent cobalt drier enhances the drying properties of this oil very much.

3. Physical Properties. The oil is light in color, being very little darker than the oil from which it is made. It will gel when allowed to stand. This gel can be melted and carried into solution, but it becomes more unworkable as it ages.

a. Solubility - This oil is extremely soluble. It will go into solution in almost any organic solvent in all proportions. A notable exception of this is ethyl alcohol, which can only be tolerated in the presence of some other solvent. A partial list of complete solvents is given below:

1. Benzol
2. Toluol
3. Xylol
4. Petroleum Ether
5. Cellosolve
6. Acetone
7. Butanol

8. Ethyl Acetate
9. Ethyl Ether
10. Ethylene Dichloride
11. Decaline
12. Free Fatty Acids
13. V. M. & P. Naphtha
14. Partially oxidized oils, etc.

b. Drying Characteristics - The drying characteristics are the oustanding features of #101 Oil. With the aid of cobalt drier the oil will dry in 17 hours at room temperature. The resulting film is tack-free, tough, and exceptionally glossy. At increased temperatures the drying time is greatly decreased. One hour at 50°C. is sufficient to give a dry film, while at 100°C. 20-30 minutes suffice. On aging, this film toughens up, retaining its gloss. If the oil is flowed in a thick layer it changes into a resinous solid if heated above 50°C. for some time.

c. The Effect of Ultra-Violet Light Radiation - The oil has resistance to ultra-violet radiation as great as, and possibly greater than, that of #100 Oil. Further, a treatment with ultra-violet light will dry this oil at room temperature.

d. Miscibility with Natural and Synthetic Resins - The oil, either in solution or uncut, can be mixed with the following resins, which have first been melted and dissolved in a little solvent:

1. Bakelite-Type Resins
2. Rosin
3. Kopal
4. Ester Gum
5. Coumar-Type Resins
6. Indene Resins, Etc.

It is not, however, miscible with any of the glyptals that were tried.

e. Miscibility with Nitrocellulose - The oil is readily miscible with both A. S. and R. S. cotton in any of the viscosities that are usually used. Several lacquer formulations are given below:

15%	wet ½ sec. A. S. cotton
18%	#101 Oil
26%	toluol
36%	ethyl acetate
3%	Ansol
2%	ethyl lactate

The same formula can be used with 5-6 second cotton, but the following formula, containing butanol, was found to give better lacquer:

12%	5-6 second cotton
15%	#101 Oil
30%	ethyl acetate

18% toluol
14% butanol
7% ansol
4% ethyl lactate

This formula has 25 per cent solids, and is, on dilution to 20 per cent solids with ethyl acetate or butanol, sufficiently thin for spraying.

4. Chemical Properties. The oil has an acid value of 20-25. The iodine value of the oil varies, depending on the value of the oil used in the reaction. A drop in the iodine number of 15-20 points results from the addition of 5 per cent maleic anhydride.

THE PRODUCTION AND PROPERTIES

OF

OXIDIZED FATTY OILS

THE PRODUCTION AND PROPERTIES OF OXIDIZED FATTY OILS

Introduction

The purpose of this study is twofold:

(1) to develop a process for the production of oxidized oils, and

(2) to study the important properties of these oxidized oils.

The interest in the field of oxidized oils is occasioned by their similarities to chinawood oil and to #100-oil. Chinawood oil is widely used in the production of gum and synthetic resin varnishes, and brake lining saturants. Despite its relatively high price and unstable supply, it enjoys wide popularity because of three unique characteristics:

(1) It is the only unprocessed oil which will permanently dissolve many types of synthetic resins,

(2) It imparts a high degree of water-resistance to varnish films, and

(3) It heat-bodies rapidly.

The #100 oil, likewise, possesses rapid drying properties, but its production is time-consuming, and its viscosity is too great for many industrial applications. Furthermore, it is incompatible with many varnish solvents.

Partially blown oils, being intermediates between raw oils and #100-oil, may possess all the desirable characteristics of the latter with none of the undesirable properties of viscosity, time and cost of production. Furthermore, they may possess the unique properties of chinawood oil, at least in a modified degree.

Taylor (465) studied the production of #100-oil and laid the basis for this work through his study of the property changes during the blowing process. In Figures 1 and 2, I have reproduced his results in graphical form.

From these results comes the suggestion of a rapid, accurate method of following the course of the blowing reaction, namely the change in refractive index. As a matter of convenience, the designation "point" has been given to an increment in refractive index of 0.0001; the designation "index oil" has been assigned to these partially oxidized fatty oils. Thus, a 40-point index oil is an oil which has been blown until its refractive index increased 40 points in the fourth decimal place.

In this investigation, the field of oxidized oils includes two main divisions:

(1) Oxidation by means of air percolation, and

(2) Oxidation by means of air or oxygen under pressure.

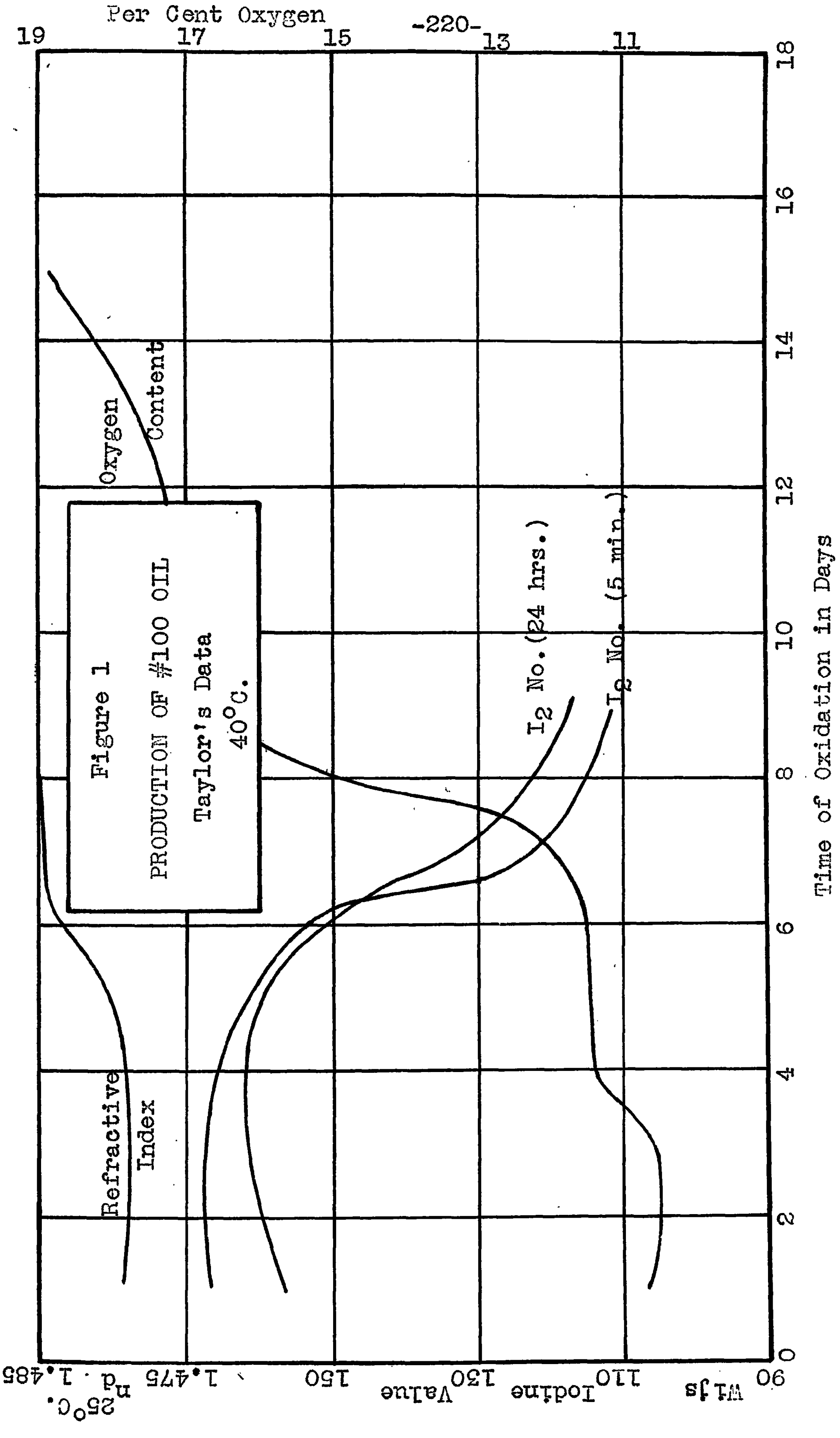


Figure 1

PRODUCTION OF #100 OIL

Taylor's Data

40°C.

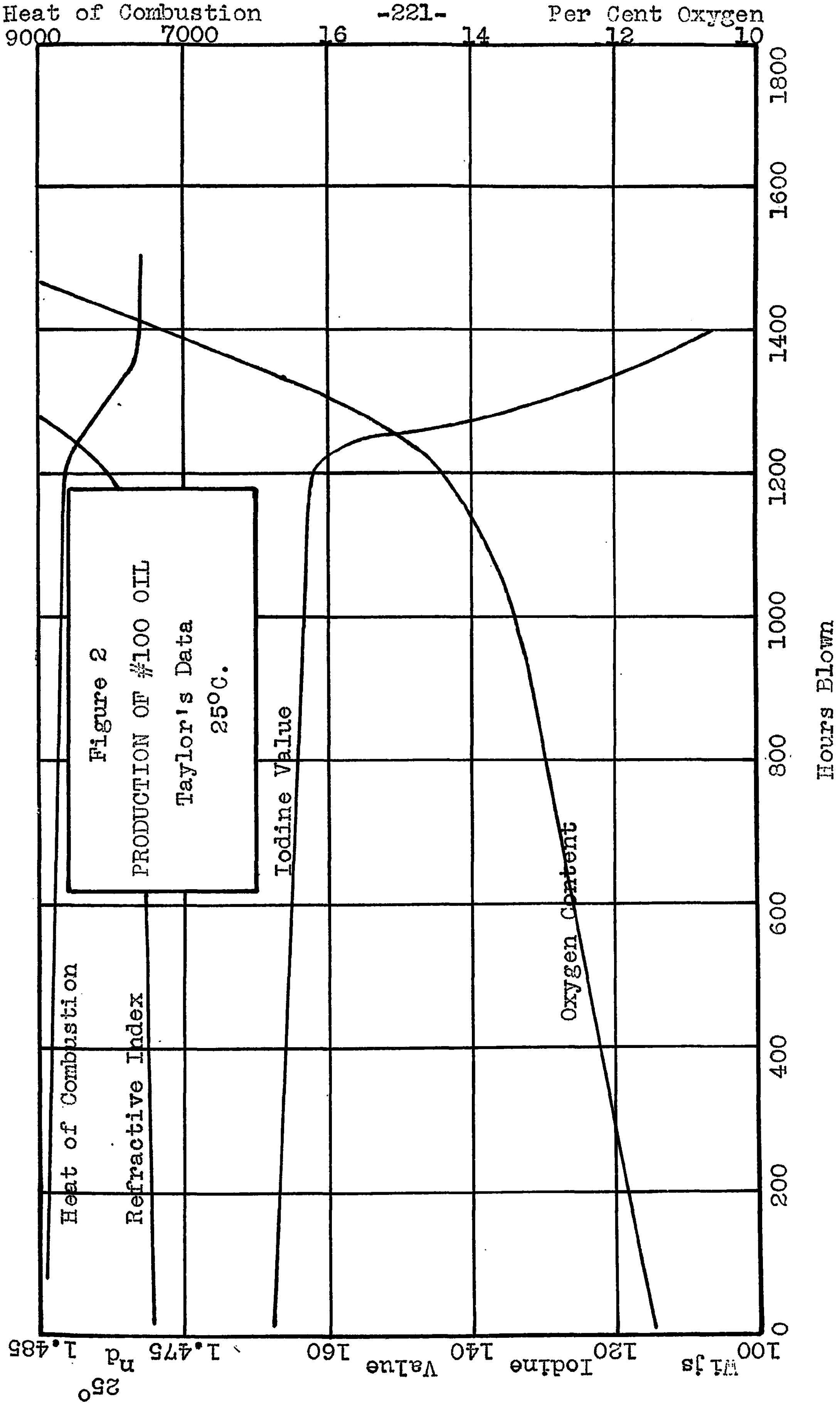


Figure 2
PRODUCTION OF #100 OIL
Taylor's Data
25°C.

APPARATUS

I. Percolator Blowing

The essential apparatus for this phase of study consists of the following:

(1) Oil containers: Glass percolators of various sizes from 2 quarts up to 3 gallons capacity.

(2) Air bubblers: Fritted glass funnels.

(3) Foam suppressors: Air jets or mechanical stirrers.

(4) Heating units: Electric light bulbs or rheostat-controlled electric heating coils.

(5) Air supply: A $\frac{1}{2}$ H.P.-60 cycle-2 phase motor compressor and accessory valves and pipe lines.

(6) Air purifier: An absorption bottle containing cotton waste.

II. Pressure Oxidation

The essential apparatus for this phase of study consists of the following:

(1) Autoclave: Aminco Bomb-Shaker 406-25, complete with heater, motor, shaking mechanism, pressure gauge, combined inlet and bleeder valve, and a 3000 ml. heat-resistant alloy steel bomb.

(2) Oil container: A stainless steel liner for the above autoclave.

(3) Temperature measurement: A chromel-X-copel thermocouple and a millivoltmeter.

(4) Gas supply: Oxygen and nitrogen gases in cylinders under pressure.

Photographs of the set-up used in the pressure oxidation of oils are shown on the following page. Figure 3 shows the inlet bleeder valve, the pressure and temperature controls, and the rocking mechanism. Figure 4 shows the head of the autoclave bomb and the thermocouple-millivoltmeter apparatus.

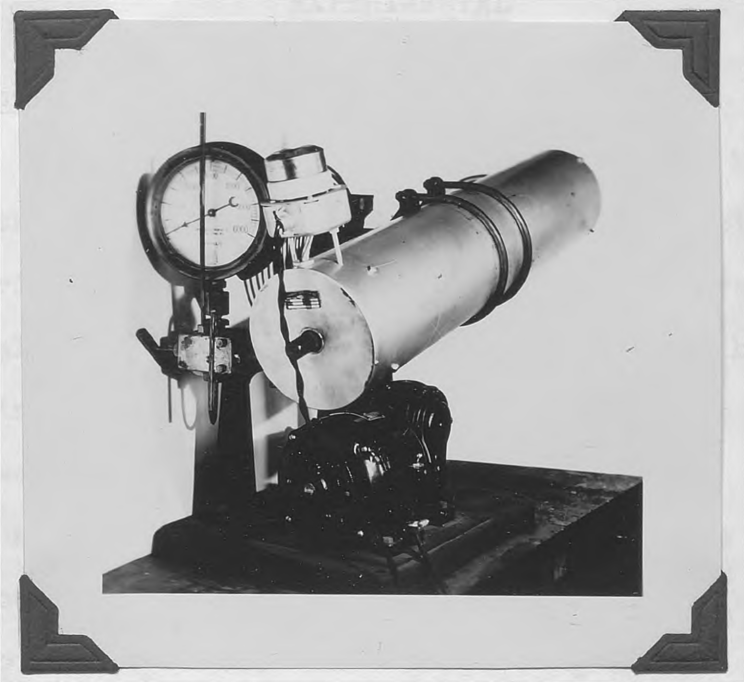


Figure 3

Figure 4

EXPERIMENTAL

Percolator Blowing

Air, usually at room temperature and humidity, is passed through cotton waste to remove grease, oil and dirt. This purified air is blown at a predetermined rate through oil samples contained in glass percolators and heated by suspending rheostat-controlled heating coils or standard size electric light bulbs directly in the oil. The fritted glass funnels disperse the air into many minute bubbles, thus providing intimate surface contact at a large number of gas-oil interfaces. This dispersing action also tends to promote agitation and even heat distribution throughout the oil. During the blowing process, the oil tends to foam, and in certain cases would overflow the apparatus and cause a large loss of sample if no precautions were taken. Air jets directed down and across the foaming oil or mechanical stirrers of low propellor pitch are used to break the foam and prevent undue losses of sample. The oil is blown in this manner until it has attained the desired properties of refractive index, iodine number, viscosity or resin solubility. Any one of these variables may be used as controls, but the refractive index has been found to be the most convenient. In particular runs, variations can be made in the oil used, the temperature, the air humidity, and the catalysts; these results will be discussed later.

Pressure Oxidation

Weighed samples of oil are measured into the autoclave liner. The autoclave head is carefully closed by gradually tightening the retaining bolts; the various line connections are tightened after the sleeves are inspected to insure proper closure. By means of the bleeder intake valve, pressure is built up in the cylinder to the desired point; the source of pressure is the usual compressed gas cylinder of nitrogen and/or oxygen, as the case may be. At the same time, the thermocouple is inserted into the well at the autoclave head and is adjusted to zero reading on the millivoltmeter. The degree of heat is controlled by a three-step heating coil and a series of two rheostats. As soon as the desired pressure is reached, the inlet valve is closed and the motor shaker is started; a slight increase in agitation may be obtained by using a spiral aluminum coil in the liner of the autoclave. The oxidation process is controlled by the pressure drop, which can be readily correlated with refractive index and other properties. When the desired pressure drop is attained, the pressure is released and the oil sample is removed for further testing. As in the percolator blowing of oils, variations in the oil, the gases and the catalysts may be made.

ANALYTICAL

Refractive Index

The refractive index of the oil was determined by means of an Abbe-Zeiss refractometer, and the readings corrected to 25° C., using the factor 0.000038 units per degree difference in temperature.

Viscosity

The viscosities of the samples were measured in both the Saybolt Standard Universal and the Saybolt Standard Furol viscosimeters, and then converted into absolute viscosities by the following formulae:

$$KV = At - Bt$$

where: KV = Kinematic viscosity
A = 0.00216 for the Universal
= 0.02040 for the Furol
B = 1.8 for the Universal
= 1.6 for the Furol
t = Time of efflux of 60 cc.

and,

Absolute viscosity = (KV) x (Specific gravity of the oil at the temperature of test)

Rapid determinations of viscosity were made with the Gardner-Holt bubble viscometer. The time of ascent of a standard-size bubble in the oil is compared with that of standardized samples of petroleum oils. The results are expressed as alphabetical viscosities, but can be easily converted to standard c.g.s. units. Care must be taken to see that the sample and the standards are at the same temperature, preferably 25° C.

Molecular Weight

For the determination of molecular weights, the usual freezing point apparatus was used. The sample was weighed into the inner test tube and was dissolved in benzene, the freezing point of which had been previously determined. Experience has shown that the best results are obtainable with samples weighing between 1.5000 and 1.7500 grams.

Resin Solubility

A mixture of 5 grams of oil and 5 grams of resin #451 was slowly heated to 200° C. Every 20° temperature rise, samples were withdrawn on the end of a thermometer and dropped on aluminum foil for visual examination of turbidity. Resin #451 is a synthetic, heat-convertible cresol-formaldehyde polymer. It is prepared as follows: one mole of cresylic acid (principally the ortho, para mixture) is acid condensed with 0.6 moles of formaldehyde. The resin is partially dehydrated, and hexamethylene tetramine is added at low temperature in order to raise the phenol/ methylene ratio to 1/1.1. The hexa acts further as a basic catalyst to produce the final resin which is soluble in oils of the tung oil type, but insoluble in linseed and other oils containing non-conjugated double bond systems.

Color

Color was tested by visual examination and comparison with standard color samples.

Drying Time

Standard panels were prepared by dipping strips of aluminum foil at definite rates of immersion. These test strips were suspended in a well-insulated drying cabinet, kept at constant temperature (100° F.) by means of an electric light bulb. The condition of tackiness was qualitatively observed until the film surface and the edge were tack-free. Only comparative tests were made.

Acid Value

The acid values were determined by titrating the sample of oil, dissolved in a mixture of ether and alcohol, with alcoholic potash. However, the samples were, for the most part, rather dark, and the end point was determined with difficulty. For this reason, several samples were checked with sodium methyl alcoholate, which gives a very distinct endpoint. These results were found to check within a few tenths of one per cent.

Iodine Value

Iodine values were determined by either the well-known Wijs' method, or by the method of Bolton and Williams (470). The latter method employs a solution of pyridine sulfate dibromide in glacial acetic acid instead of the iodine monochloride of Wijs' method. Bolton-Williams determinations have been shown to be more accurate for blown oils (462), as the solution does not react with the ordinary groups (hydroxy, keto, etc.) thought to be present in blown oils.

Ultimate Analysis

Determinations of the oxygen percentage of blown oils was made by the Liebig combustion method, absorbing the water in dehydrite reagent (anhydrous $MgClO_4$), and the carbon dioxide in ascarite (NaOH-asbestos). Extreme care must be used in the early stages of the combustion of blown oils because of their foaming and exploding tendencies. During these early stages, the heat must be lower than usual, and the supply of oxygen must be much more rapid than usual. Otherwise, no special difficulties were experienced.

RESULTS

Production of Percolator Blown Oils

(1) Blowing of various oils - In these runs, oils were blown at 40° C. with ordinary laboratory air from which dirt and oil had been removed. Only typical examples of each run are tabulated because of the similarities in repeated runs. The following oils were blown:

(a) Superb linseed oil - an alkali-refined oil.

(b) Non-break, raw linseed oil - an oil in which only the kettle break is removed from the oil.

(c) SH'd linseed oil - an oil from which practically all the break has been removed without affecting the acid number.

(d) Superb soyabean oil - an alkali-refined oil.

(e) Non-break perilla oil - an oil in which only the kettle break is removed from the oil.

(f) Light-pressed, refined menhaden oil - an oil in which both the foots and the kettle break are removed.

In most cases, only the change in refractive index was recorded. The curves and data for typical runs on each oil are tabulated on the following pages.

TABLE I

Blowing of Superb Linseed Oil*

Sample Number	Elapsed Time, Hours	$n_D^{25^\circ}$	Remarks
1	0	1.4780	Light-colored oil
2	9	1.4781	
3	20	1.4782	
4	28	1.4784	
5	35	1.4784	
6	42	1.4784	Bleaching action
7	46	1.4787	
8	50	1.4793	
9	55	1.4805	
10	60	1.4811	
11	65	1.4814	
12	72	1.4815	Resin solubility

* Data plotted in Figure 5.

In the blowing of Superb linseed oil at 40° C., there is a definite induction period during which the oil undergoes only slight, if any, changes in its properties. At the end of this induction period, which is approximately 44 hours in duration, there is a very rapid but short-lived change in properties. From the data of Taylor (loc. cit.) we know that these rapid changes in properties take place after the start of a rapid take-up of oxygen. A plot of iodine value and acid value against the percentage of oxygen in the sample is shown in Figure 6 in order to emphasize the exceedingly short life of these rapid changes.

The blowing reaction is exothermic in this and in every other run, but varies somewhat in degree according to the type of oil being blown, and is proportional to the

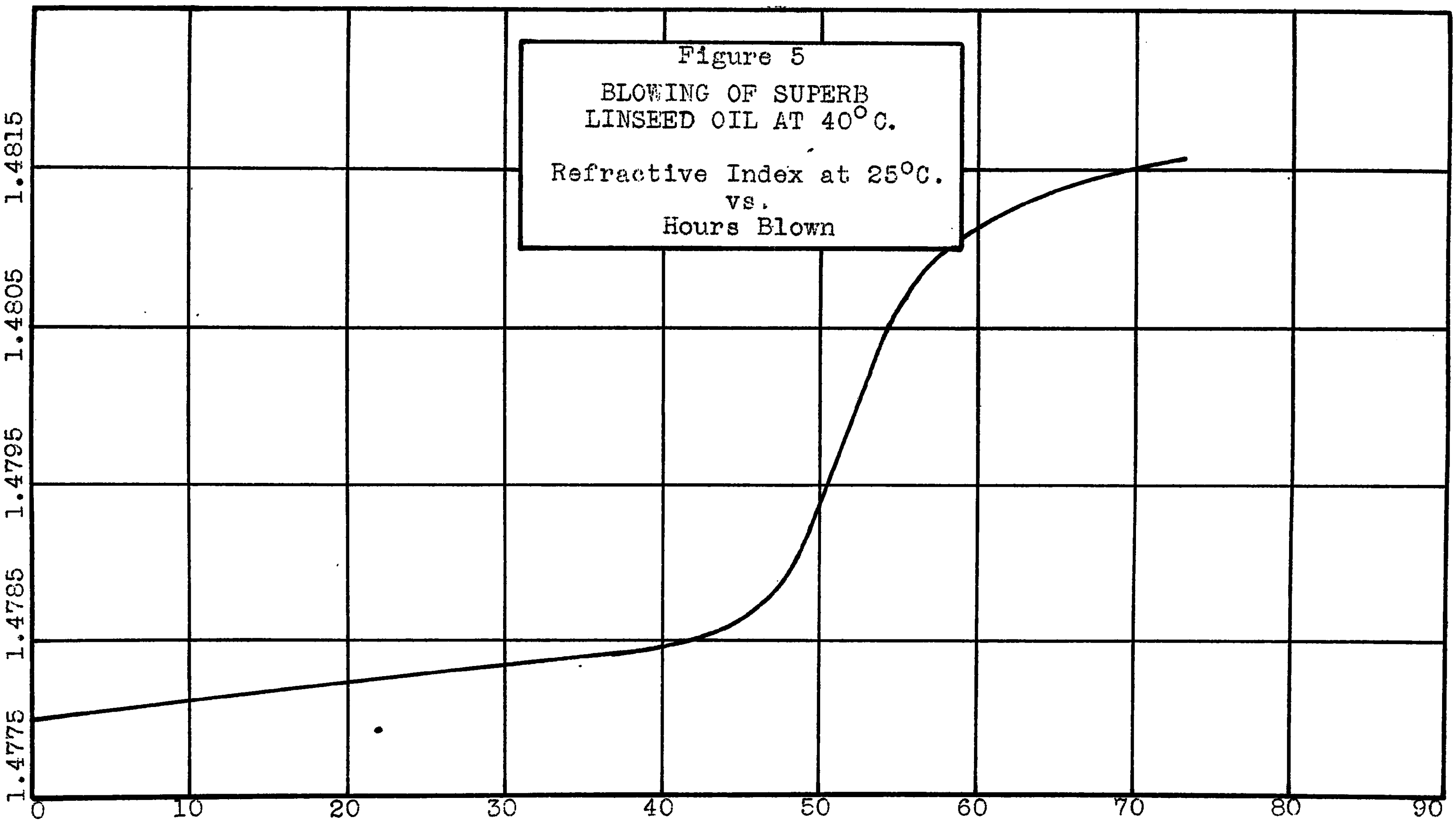


Figure 5

BLOWING OF SUPERB
LINSEED OIL AT 40° C.

Refractive Index at 25°C.
vs.
Hours Blown

degree of unsaturation of particular acid residues forming the oil glycerides.

TABLE II

Blowing of SH'd Linseed Oil*

Sample Number	Elapsed Time, Hours	$n_D^{25^\circ}$	Remarks
1	0	1.4715	Dark oil
2	3	1.4715	
3	10	1.4717	
4	15	1.4721	Very little bleaching action
5	17	1.4721	
6	20	1.4721	
7	25	1.4722	
8	31	1.4724	
9	35	1.4726	
10	38	1.4728	
11	40	1.4731	
12	44	1.4736	
13	50	1.4748	Resin solubility
14	53	1.4751	
15	55	1.4757	Resin solubility

* Data plotted in Figure 7.

Sh'd linseed oil blows at a much more rapid rate. There are apparently two induction periods, the second of which is relatively short in duration. Unlike most of the other oils, Sh'd oil exhibits either no bleach point or only a very slight bleaching action.

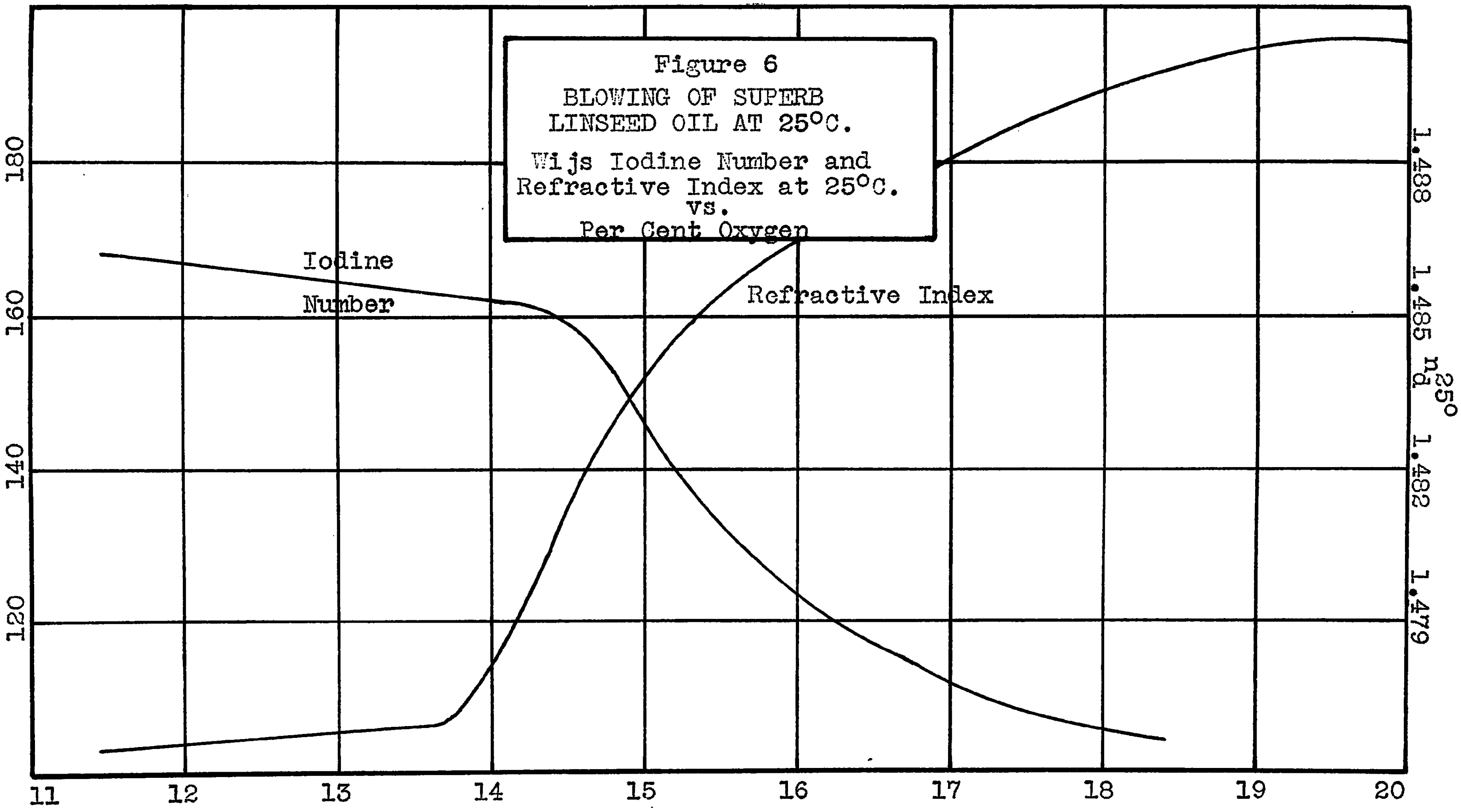


Figure 6

BLOWING OF SUPERB
LINSEED OIL AT 25°C.

Wijs Iodine Number and
Refractive Index at 25°C.
vs.
Per Cent Oxygen

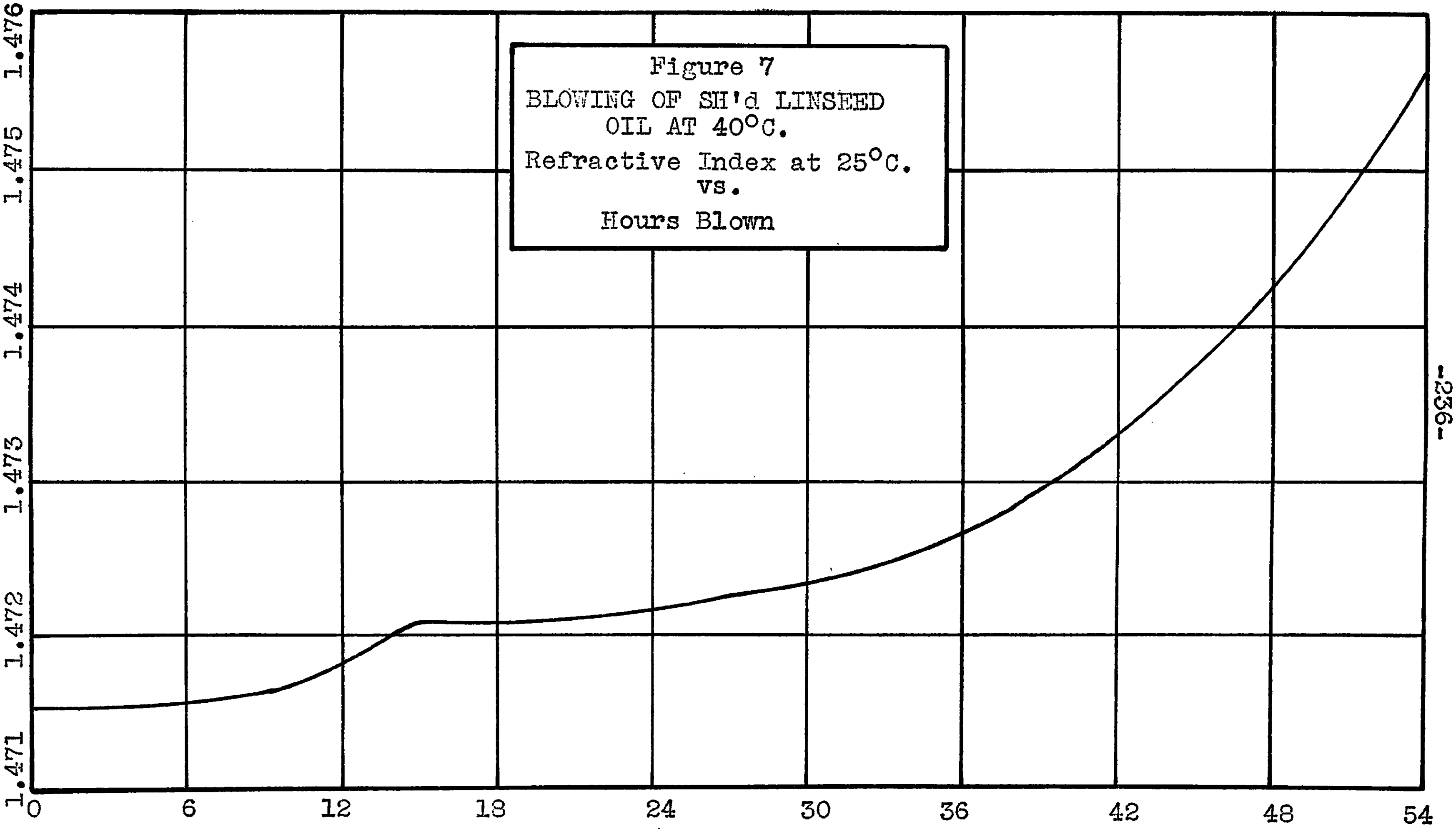


Figure 7
BLOWING OF SH'd LINSEED OIL AT 40°C.
Refractive Index at 25°C.
vs.
Hours Blown

TABLE III

Blowing Of Superb Soyabean Oil*

Sample Number	Elapsed Time, Hours	$n_D^{25°}$	Remarks
1	0	1.4737	Very light-colored oil
2	5	1.4737	
3	11	1.4738	
4	15	1.4740	
5	18	1.4744	
6	21	1.4745	
7	23	1.4744	
8	30	1.4745	
9	38	1.4746	
10	45	1.4746	
11	57	1.4747	
12	60	1.4746	Strong bleaching action
13	72	1.4750	
14	75	1.4754	
15	83	1.4763	
16	90	1.4776	Resin solubility
17	91.5	1.4781	Resin solubility

* Data plotted in Figure 8.

In the blowing of soyabean oil, two distinct induction periods are present. After blowing has proceeded for a short time, there is a rise in refractive index. The increase is only slight, however, and then a second induction period sets in. After a few more hours, the oil begins to bleach, even though it is quite light in color originally. Simultaneously with this bleaching, the temperature of the oil tends to rise, and the refractive index increases very rapidly.

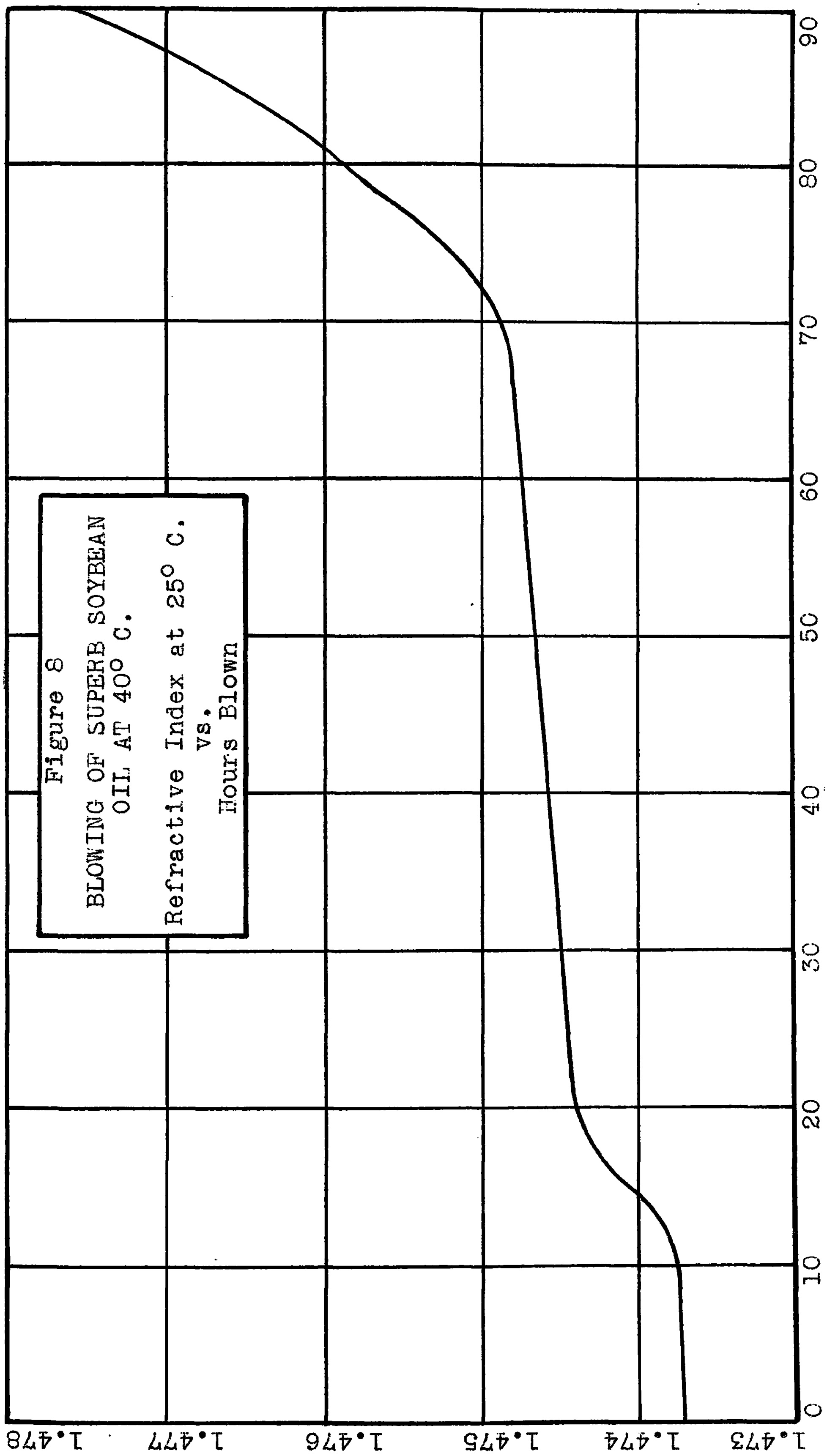


Figure 8

BLOWING OF SUPERB SOYBEAN OIL AT 40° C.

Refractive Index at 25° C.
vs.
Hours Blown

TABLE IV

Blowing of Non-Break Perilla Oil*

Elapsed Time, Hours	Temp. °C.	$n_D^{25°}$	Wijs I_2 No.	Remarks
0	40	1.4810	203	Pale yellow, clear.
3	44	1.4809		
20½	41	1.4810	204	Very slight foaming.
23	42.5	1.4810		
25	43	1.4809		
28	46	1.4810		
29½	35	1.4810		
31½	39.5	1.4811		
34½	42.5	1.4812		
38	41.5	1.4812		
41	40.5	1.4813		
44	41	1.4812		
47	43	1.4813		
51	43	1.4814		
56	38.5	1.4814		Color slightly lighter.
60	38.5	1.4815		
64	42.5	1.4815		
67	41.5	1.4817		
69	42	1.4816	202.5	
71	41	1.4815		
73½	41	1.4815	201	
76½	41.5	1.4816		
79½	40.5	1.4818		Somewhat bleached.
81½	39.5	1.4822		
83	40.5	1.4823	195.4	
84	23.5	1.4827		
85½	39.5	1.4830		
88½	43.5	1.4836		
90	38	1.4840		No resin solubility.
92	41.5	1.4843		
94½	42	1.4845	176.8	
96½	42.5	1.4850		
98½	41.5	1.4856		
101	40	1.4865		Resin solubility.
102½	39.5	1.4870	163	
105	40	1.4874		
107	42.5	1.4879		Very viscous.
110	37	1.4885	148.0	Pale, very aerated.
112	37.5	1.4889		
114	37	1.4895		Extremely viscous.
117	39.5	1.4897	140.8	Forms tenacious.
120	40	1.4898	132.7	Film on refractometer.

* Data plotted in Figure 9.

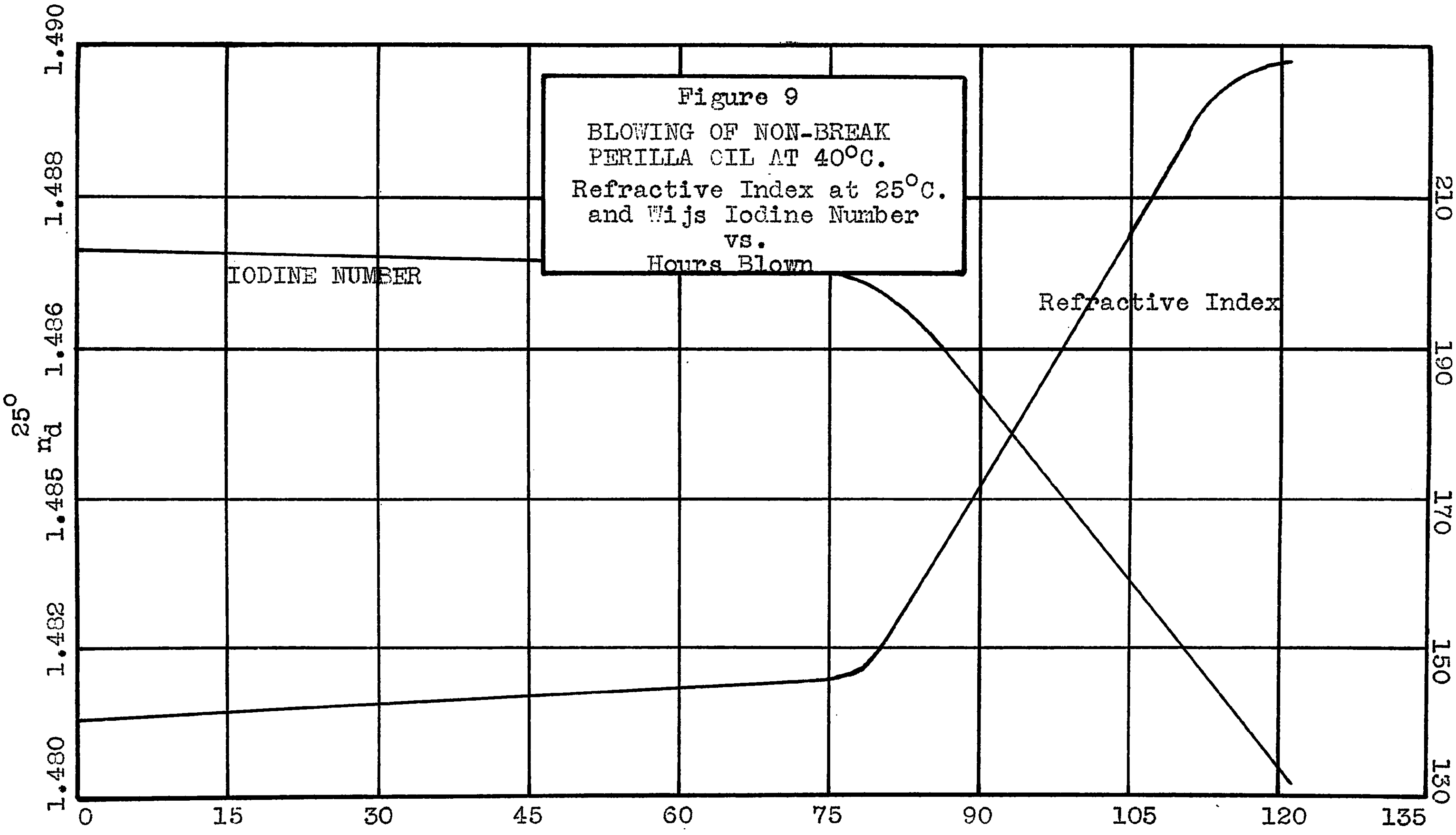


Figure 9

BLOWING OF NON-BREAK
PERILLA CIL AT 40°C.

Refractive Index at 25°C.
and Wijs Iodine Number
vs.
Hours Blown

After a long induction period of about 74 hours, there is a rapid change in refractive index and iodine number along with the simultaneous development of viscosity and resin solubility. After 120 hours of blowing, the oil is practically gelled, and has a much lighter color than the original oil.

TABLE V.

Blowing of Refined Menhaden Oil*

Elapsed Time, Hours	Temp. °C.	$n_D^{25°}$	Wijs I_2 No.	Remarks
0	22	1.4784	184.0	Foaming.
4½	47	1.4790	179.6	
22½	64	1.4823	138.4	Acrolein formed; much foaming.
25½	49	1.4829	139.4	Very viscous.
28½	62	1.4834	119.8	Resin solubility.
32	50	1.4841		
35	57	1.4847	114.3	Less foaming.
38	58	1.4852	111.2	No acrolein effect; almost a gel.
41½	48	1.4854	107.3	
45	47	1.4854		Gel-like.

* Data plotted in Figure 10.

The blowing curves of this oil are unique in three particulars:

(1) There is no induction period,

(2) There is an excessive rise in temperature, and

(3) There is an excessive evolution of acrolein-like fumes.

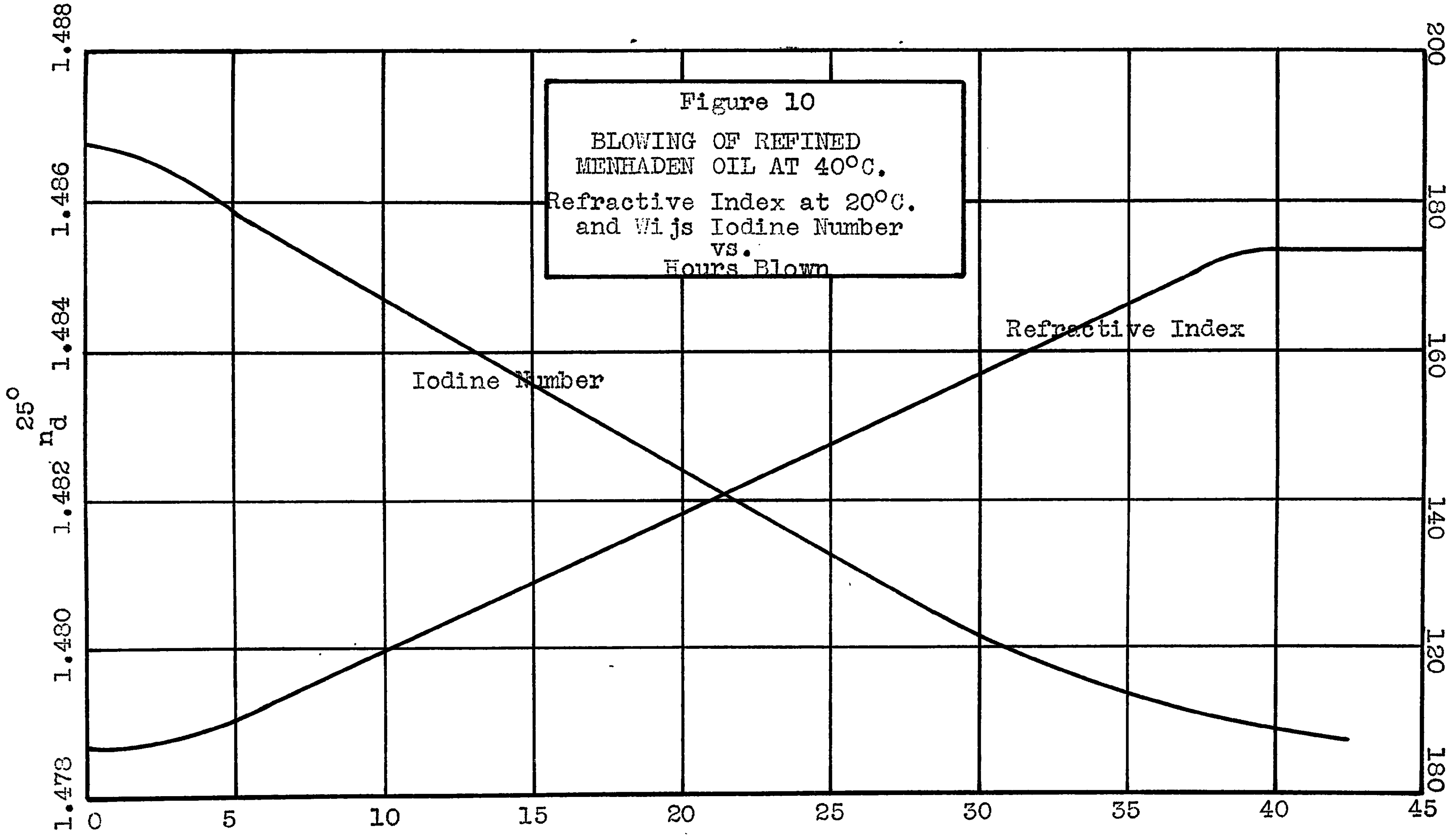


Figure 10

BLOWING OF REFINED
MENHADEN OIL AT 40°C.

Refractive Index at 20°C.
and Wijs Iodine Number
vs.
Hours Blown

Undoubtedly, these distinctions are partially due to the presence of the highly unsaturated clupanodonic acid, which readily oxidizes, decomposes and polymerizes. In addition, the natural oil antioxidants have been largely removed during the refining process.

For purposes of comparison, the changes in refractive index for these five oils have been plotted against blowing time in Figure 11.

(2) Effect of Temperature - Experiments have shown that the higher the temperature at which an oil is blown, the more rapidly it reaches a given value of refractive index. Unfortunately, the viscosity is abnormally increased at higher temperatures of blowing. The effect of temperature is shown in curves A and B of Figure 12. The results of curve A were obtained by maintaining the temperature of blowing very carefully at 50° C., while the temperature of blowing in curve B varied between 30° C. and 50° C. In both cases, samples of Superb linseed oil from the same batch were used. At temperatures approaching 200° C., a blown oil, having none of the desirable properties of index oil, is produced.

(3) Effect of Air Humidity - In these runs, the temperature of blowing was increased to 75° C. in order to shorten the time to a convenient period. Four samples of

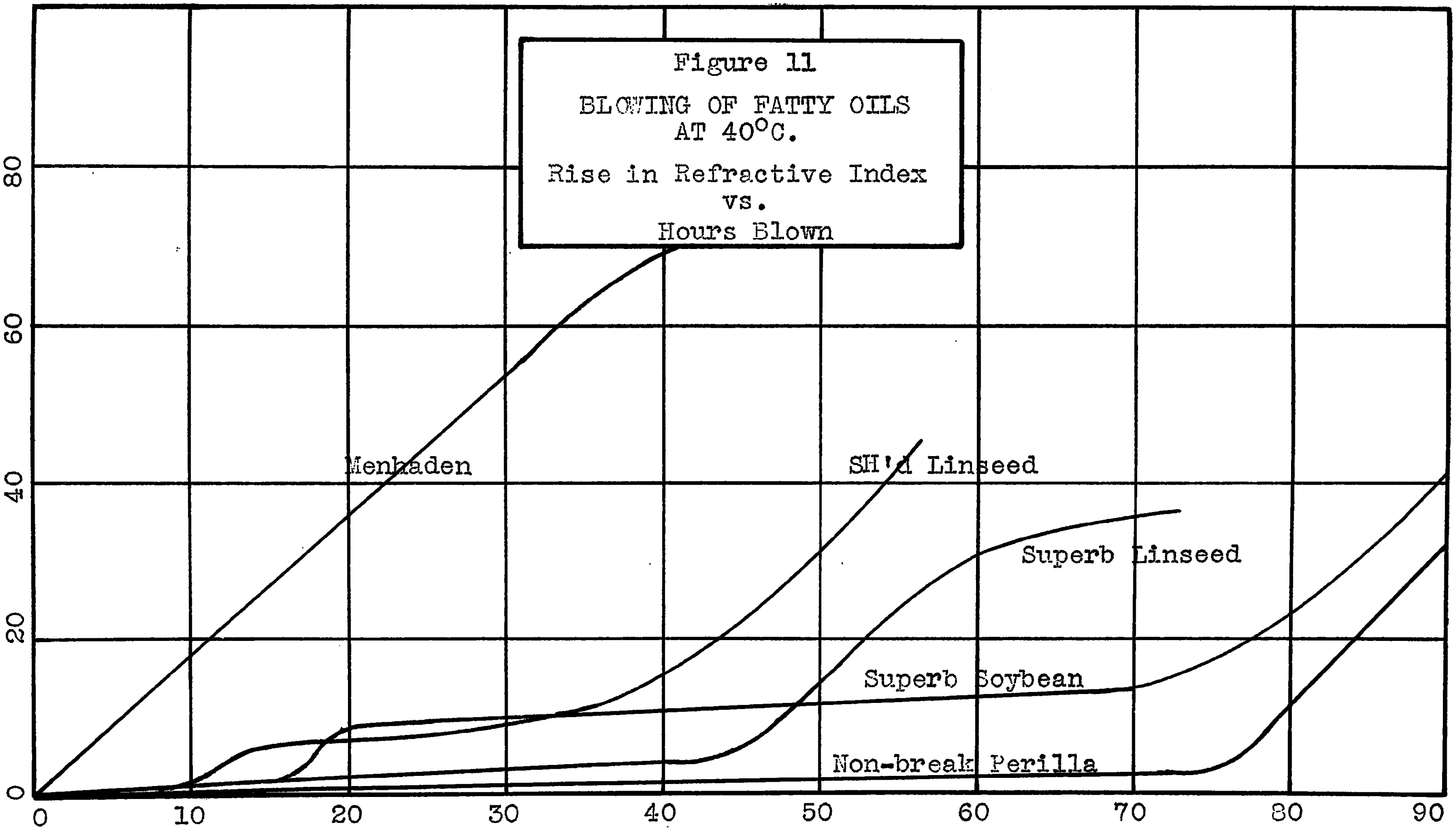


Figure 11

BLOWING OF FATTY OILS
AT 40°C.

Rise in Refractive Index
vs.
Hours Blown

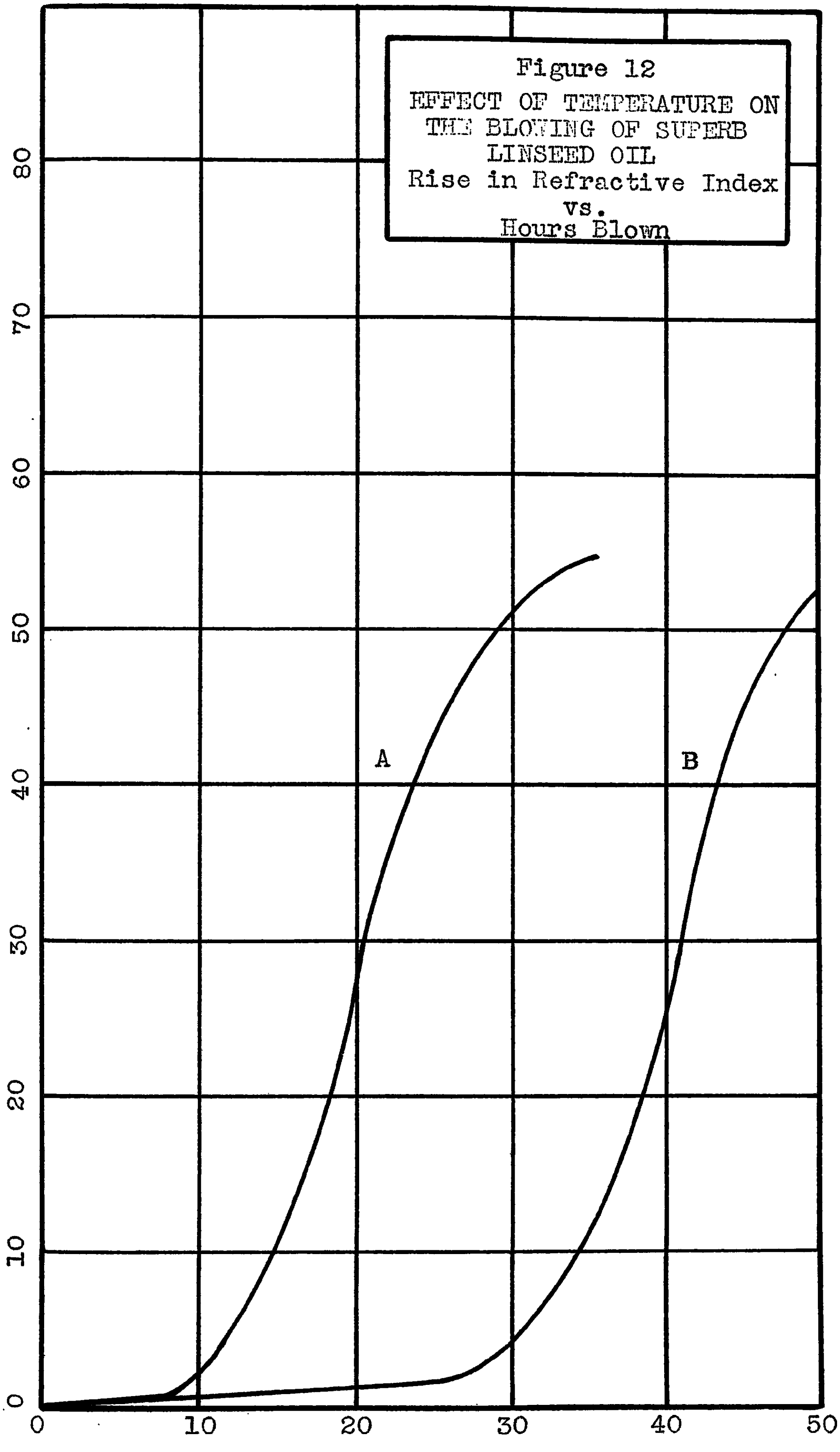


Figure 12
EFFECT OF TEMPERATURE ON THE BLOWING OF SUPERB LINSEED OIL
Rise in Refractive Index vs. Hours Blown
A
B
0
10
20
30
40
50
60
70
80
0
10
20
30
40
50

oil were blown, using air of different percent moisture, viz.:

(a) Dry air - dried by bubbling through concentrated sulfuric acid in a bubbling tower,

(b) Ordinary air of intermediate humidity,

(c) Saturated air - air bubbled through water in a bubbling tower, and

(d) Saturated air and water added directly to the system.

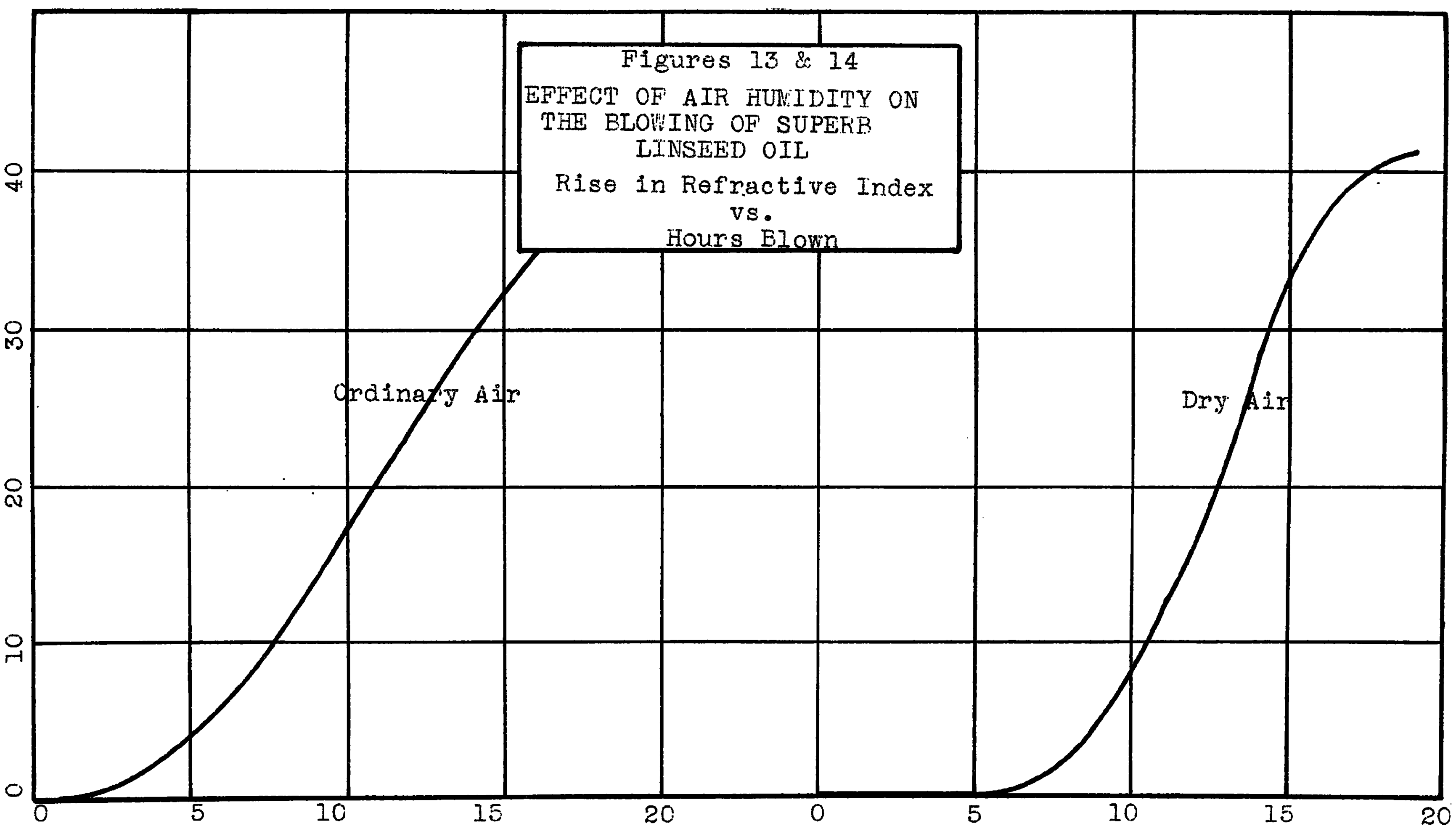
Refractive indices were observed throughout the duration of the run. Acid values were determined at the beginning and end of each run. The moisture content of the air was obtained by the use of a wet testmeter and drierite tube connected in parallel with the air line. The data for these runs is tabulated in Tables VI. to IX., and in Figures 13 to 16 respectively.

TABLE VI.

Superb Linseed Oil Blown With Dry Air

Time of Blowing (Hours)	Refractive Index	Rise
0	1.4711	0
2	1.4711	0
5	1.4711	0
8.75	1.4715	.0004
10	1.4725	.0014
12.5	1.4725	.0014
14.0	1.4739	.0028
15.75	1.4748	.0037
16.75	1.4749	.0038
17.75	1.4751	.0040

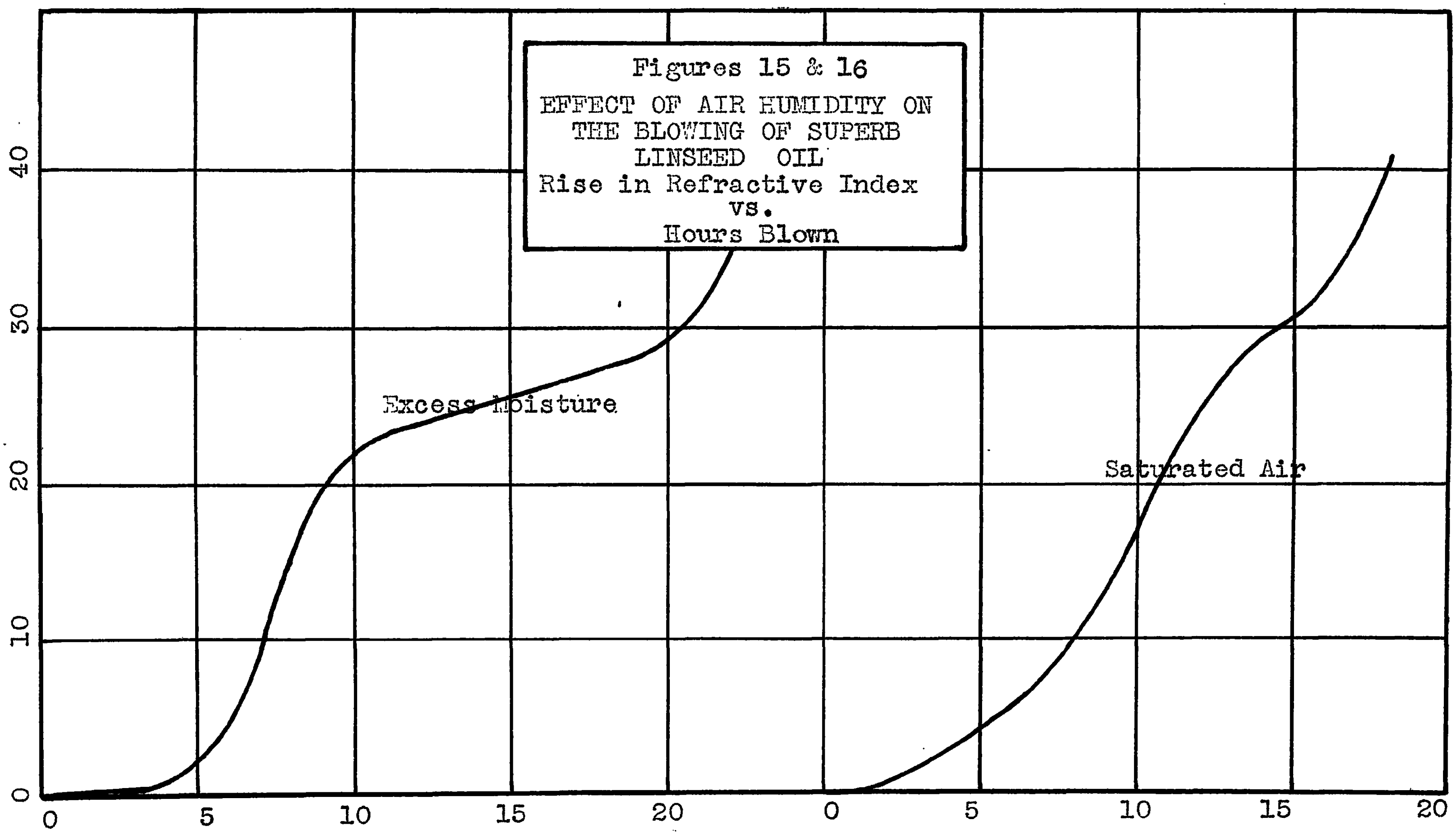
Total time of blowing - 17.75 hrs.   Acid No. (before) - .403
Average temperature - 75° C.   Acid No. (after) - 3.33
Humidity - 0.000238# water/# air



Figures 13 & 14

EFFECT OF AIR HUMIDITY ON THE BLOWING OF SUPERB LINSEED OIL

Rise in Refractive Index
vs.
Hours Blown



Figures 15 & 16

EFFECT OF AIR HUMIDITY ON THE BLOWING OF SUPERB LINSEED OIL

Rise in Refractive Index
vs.
Hours Blown

TABLE VII.

Superb Linseed Oil Blown With Ordinary Air

Time of Blowing (Hours)	Refractive Index	Rise
0	1.4795	0
1.5	1.4795	0
4	1.4800	.0005
5	1.4802	.0007
6	1.4805	.0010
7	1.4806	.0011
9	1.4815	.0020
9	1.4818	.0023
10	1.4821	.0026
11	1.4823	.0028
12	1.4825	.0030
13	1.4828	.0030
14	1.4936	.0041

Total time of blowing - 14 hours   Acid No. (before) - .403
Average temperature - 80° C.   Acid No. (after) - 5.00

Humidity (average) - .0065# water/# air

TABLE VIII.

Superb Linseed Oil Blown With Saturated Air

Time of Blowing (Hours)	Refractive Index	Rise
0	1.4795	0
1.5	1.4795	0
4	1.4800	.0005
5	1.4800	.0005
6	1.4802	.0007
7	1.4805	.0010
8	1.4815	.0020
9	1.4820	.0025
10	1.4821	.0026
11	1.4824	.0029
12	1.4826	.0031
13	1.4828	.0032
14	1.4836	.0041

Total time of blowing - 14 hours   Acid No. (before) - .403
Average temperature - 75° C.   Acid No. (after) - 5.67

Humidity - .0158# water/# air

TABLE IX.

Superb Linseed Oil Blown With Excess Moisture

Time of Blowing (Hours)	Refractive Index	Rise
0	1.4711	0
2	1.4711	0
5	1.4713	.0002
8	1.4730	.0019
9	1.4730	.0019
11	1.4735	.0024
15	1.4736	.0025
17.25	1.4737	.0026
20.25	1.4739	.0029
22.25	1.4739	.0029
23.0	1.4752	.0040

Total time of blowing - 23 hours Acid No. (before) - .403
Average temperature - 65° C. Acid No. (after) - 3.45

Humidity - .0124# water/# air

This data indicates that water vapor has an accelerating effect on the blowing reactions. However, excess liquid water does not seem to have any specific accelerating action, but it does tend to change the shape of the blowing curve. A plot of the acid values for dry, intermediate and saturated air blows against the humidity of the air is shown in Figure 17. Apparently the increased water content of the air induces the formation of acidic substances, probably by splitting reactions at the double bonds and at the glyceride linkages.

(4) Acceleration of Blowing - Temperature has been shown to have a strong accelerating action on the blowing of oils, but to produce at the same time oils too viscous for

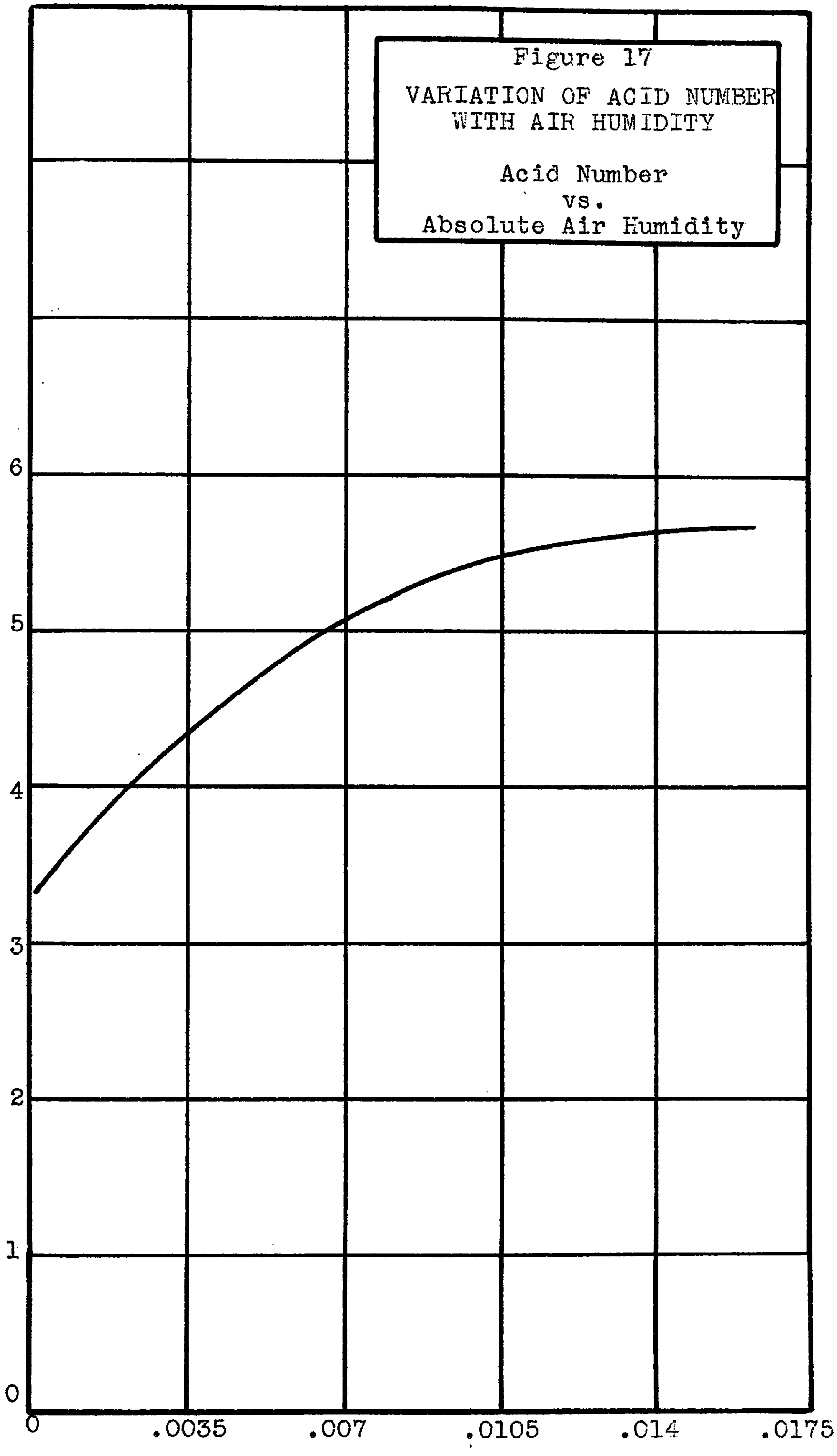


Figure 17

VARIATION OF ACID NUMBER WITH AIR HUMIDITY

Acid Number
vs.
Absolute Air Humidity

many applications. An acceleration without too large an increase in viscosity is obtained by blowing at more than one temperature.

In this method, the oil was blown at some elevated temperature (70° C.) until the end of the induction period was reached. The oil was then cooled to about 40° C., and blowing was continued until the required index was produced. In this way, a 40-point index oil was produced in 25-30 hours, where previously it had required 60-65 hours. Moreover, the product thus formed had the same viscosity characteristics as oil which had been blown continuously at 40° C. The data for the double temperature blowing of non-break, raw linseed oil is shown in Table X, ~~and plotted in Figure 18~~.

TABLE X.

Double Temperature Blow of Non-Break, Raw Linseed Oil

Sample Number	Elapsed Time, Hours	$\Delta n_D^{25^\circ}$	Temperature °C.
1	0	0	70°
2	5	0.0002	70°
3	8	0.0003	70°
4	10	0.0004	70°
5	14	0.0007	65°
6	16	0.0014	40°
7	20	0.0027	40°
8	23	0.0034	40°
9	25	0.0040	40o

A second run was made on SH'd linseed oil. The oil was blown for seven hours at 95° C., during which time

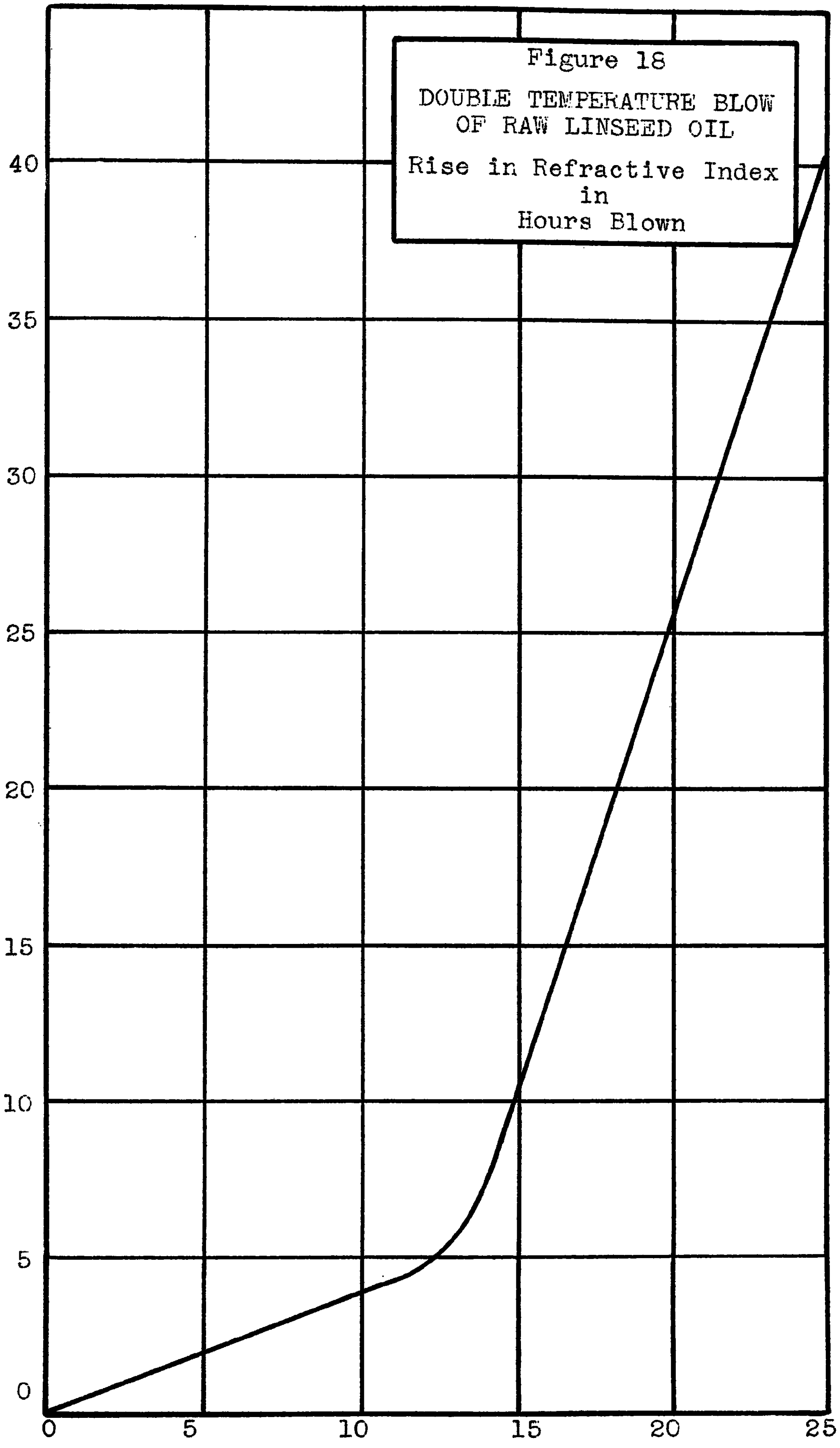


Figure 18
DOUBLE TEMPERATURE BLOW
OF RAW LINSEED OIL
Rise in Refractive Index
in
Hours Blown
40
35
30
25
20
15
10
5
0
0
5
10
15
20
25

the refractive index rose 25 points, and then was blown $3\frac{1}{4}$ hours at 70° C. The final oil had an index of 44, a value reached only after 55 hours blowing at 40° C.

One of the first suggestions for the catalysis of air blowing was the addition of blown oil in moderate amounts. Theoretically, if the blowing action is autocatalytic, then oil which contains the autocatalytic substances should initiate the blowing reactions of untreated oil. Various ratios of blown oil and unblown oil were used without any significant success. The time of blowing was not shortened to any appreciable extent unless ratios of about 50-50 were used. Since this only shortened the time of blowing about 10 per cent, there is no practical utility to the process.

The next step in the catalysis of the blowing reaction was the study of the effect of driers, in particular the naphthenate (Nuodex) soaps of cobalt, manganese and lead.

Several blows of Superb linseed oil were made with varying percentages of added drier. The blows were conducted at room temperature, using 0.001%, 0.005% and 0.01% cobalt as cobalt Nuodex. The results were as follows:

TABLE XI.

Catalyzed Blowing of Superb Linseed Oil

Catalyst Concentration (% Co as cobalt Nuodex)

0.001%		0.005%		0.01%	
Hours	$\Delta n_D^{25^\circ}$	Hours	$\Delta n_D^{25^\circ}$	Hours	$\Delta n_D^{25^\circ}$
10	9	10	29	10	33
Discontinued		15-3/4	40	12¼	40

These experiments were repeated on SH'd linseed oil, but 0.005 per cent cobalt catalyst only raised the refractive index 9 points in 45½ hours blowing at room temperature. When the temperature of blowing was increased to 35° C., a nine-point rise was obtained in 9½ hours.

These times were still slower than those for Superb linseed oil; therefore, the temperature of blowing was raised to 45° C., and the amount of drier was increased in one case to 0.01 per cent cobalt, and in another to 0.015 per cent cobalt as cobalt Nuodex. Under these conditions, a seven-hour blow produced a 32-point oil in the first case, and a 37-point oil in the second.

Although the action of cobalt salts as driers was quite satisfactory, tests were conducted using other driers. Lead, as lead Nuodex, was the first tried. A sample of Superb oil to which 0.10% lead had been added, was blown at a temperature of 50° C. for 12-3/4 hours, with a resultant rise in refractive index of 32 points. This time was considerably longer than was required when cobalt was added to blow the oil. However, the increased time was not the greatest objection, as the oil to which the lead drier had been added clouded upon blowing. The fine precipitate which caused the cloudiness did not settle upon standing, but it could be removed by thinning the oil with a solvent and centrifuging for about an hour. Sh'd oil was also blown with lead drier added, but it too became cloudy upon blowing, and the time required was again quite a bit greater than for the sample with cobalt drier added. Because of this increased blowing time and subsequent clouding of the oil, the use of single lead driers in the blowing of an oil was abandoned.

The use of manganese, as manganese Nuodex, as a catalyst for blowing was then tried. At a temperature of 50° C., a blow of Superb oil to which had been added 0.005% manganese drier indicated a change in refractive index of 34 points in 9¼ hours. Under the same conditions, the refractive index of Sh'd oil rose only three points in 7½ hours.

In the paint and varnish industry, a mixture of driers is usually preferred to a single drier, as the mixture of driers gives an oil better drying properties. For this reason, several mixtures of driers were used in the blowing of Sh'd oil. All of the blows were conducted at a temperature of 50° C. To one sample was added 0.0025% manganese drier plus 0.005% cobalt drier, to another 0.005% manganese drier plus 0.10% lead drier, and to another 0.005% cobalt drier plus 0.10% lead drier, all as metallic Nuodex driers. Forty-point index oil was produced in 4½ hours with the mixture of manganese and cobalt driers, and in 8½ hours with both the mixture of manganese and lead and the mixture of cobalt and lead driers. A mixture of 0.0025% cobalt drier plus 0.0025% manganese drier, both as Nuodex driers, was also tried, but 12 hours of blowing at 50° C. were required to produce 40-point index oil. As the mixtures of driers were so far superior to any one drier used separately, a mixture of 0.005% cobalt and 0.005% manganese driers was added to non-break raw linseed oil, and by blowing at a temperature of 50° C., a rise in refractive index of 40 points was obtained in 6½ hours. The time required to get the same change in refractive index without the addition of driers, all other conditions remaining constant, was 36½ hours.

Soyabean oil, although a semi-drying oil, was blown 40 points in 14 hours at 50° C., using 0.005% cobalt drier as cobalt Nuodex. The same oil without catalysts required 140 hours to attain a 40-point rise in refractive index.

The plotting of typical catalyzed and uncatalyzed blows of Superb linseed oil, Sh'd linseed oil, non-break, raw linseed oil and Superb soyabean oil shows the startling effect of driers more convincingly. These results are plotted in Figures 19 to 22 inclusive. Curve A of Figure 19 represents the blowing of Superb linseed oil at 50° C. without the addition of driers, while curve B represents the blowing of the same oil at 25° C. with 0.005% cobalt drier added. In Figure 20, curve A is for the blowing of SH'd linseed oil at 40° C. without added drier, and curve B is for the blowing of the same oil at 45° C. with 0.005% cobalt drier and 0.0025% manganese drier added. The blowing of non-break raw linseed oil at 50° C. without drier and with 0.005% cobalt and 0.005% manganese driers is represented in curves A and B, respectively, of Figure 21. Curve A of Figure 22 represents the blowing of soyabean oil without any added drier, while curve B represents the blowing of the same oil with the addition of 0.005% cobalt drier; both blows were conducted at 50° C.

The calculation of the induction period and maximum slope of various oils, catalyzed and uncatalyzed, shows the decided differences in blowing times quite clearly. These results have been summarized in the following table:

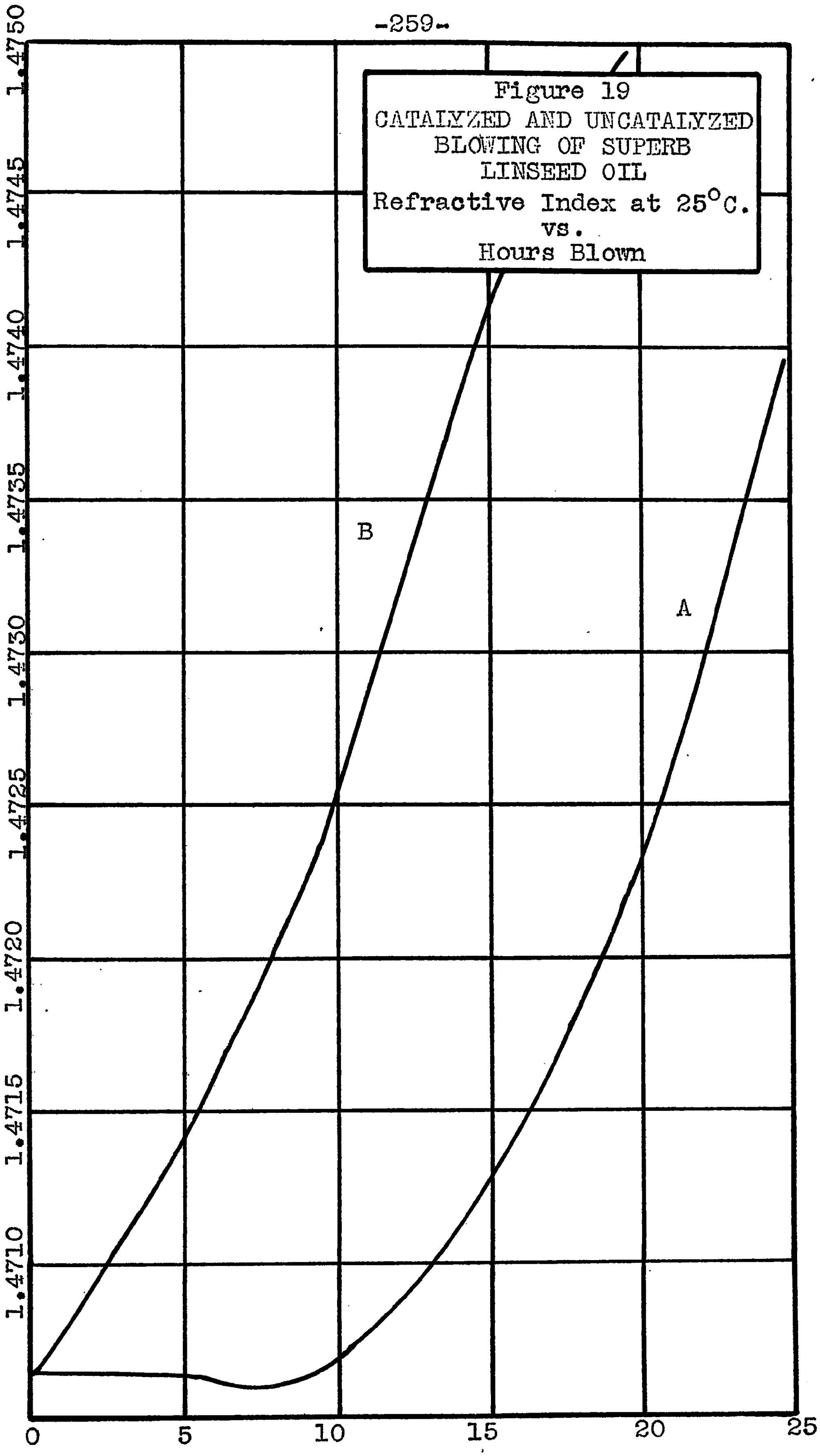


Figure 19
CATALYZED AND UNCATALYZED
BLOWING OF SUPERB
LINSEED OIL
Refractive Index at 25°C.
vs.
Hours Blown

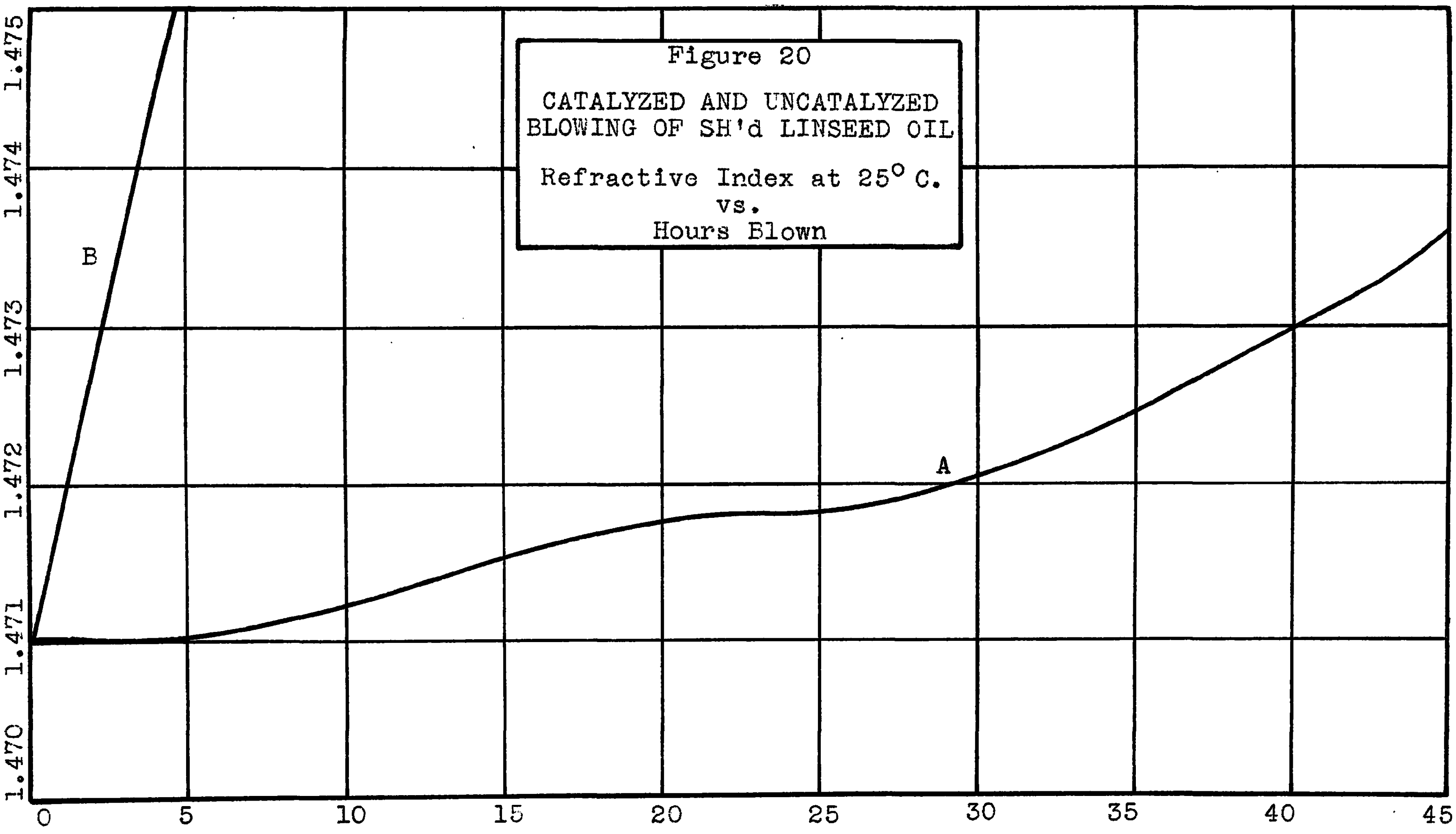


Figure 20

CATALYZED AND UNCATALYZED
BLOWING OF SH'd LINSEED OIL

Refractive Index at 25° C.
vs.
Hours Blown

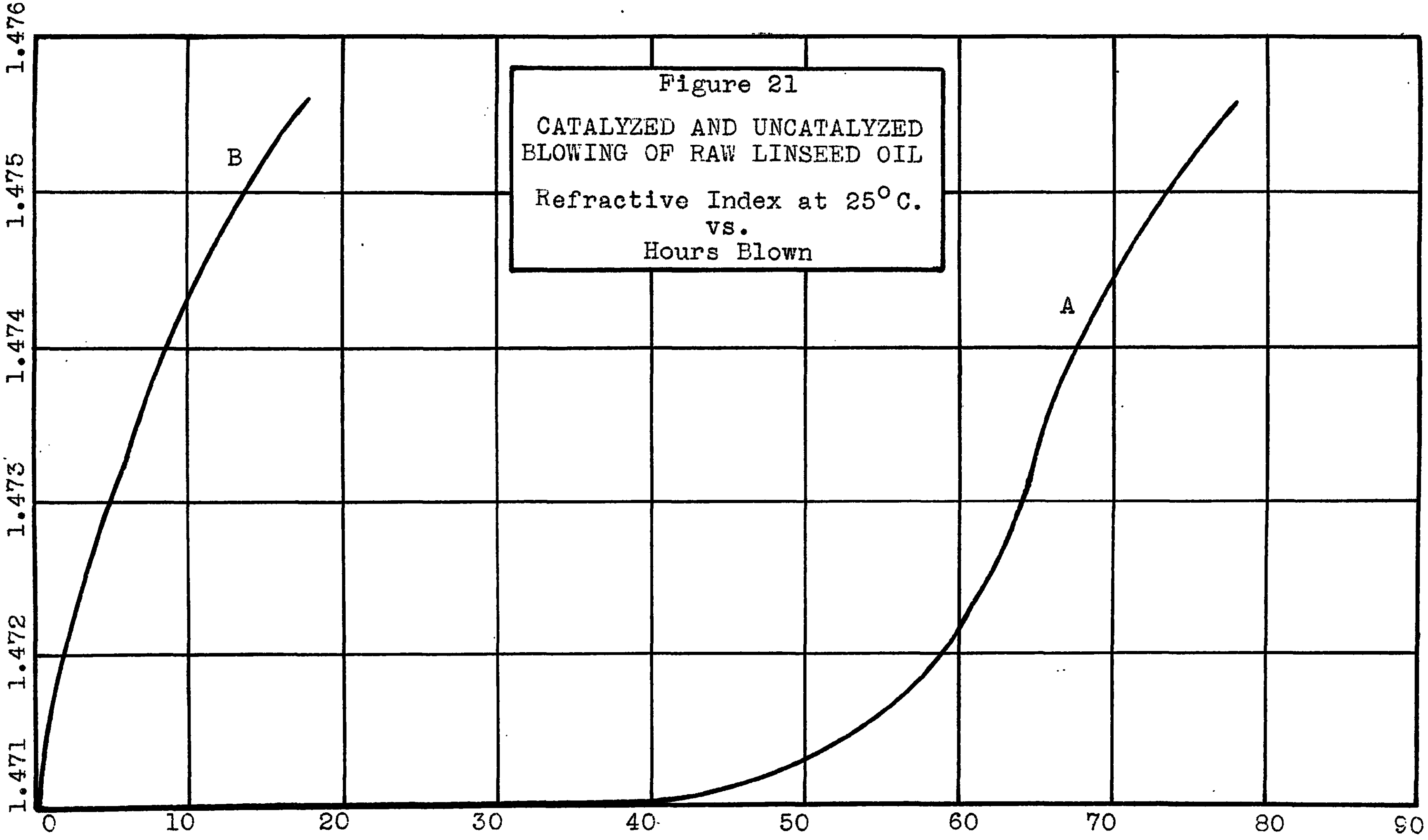


Figure 21

CATALYZED AND UNCATALYZED
BLOWING OF RAW LINSEED OIL

Refractive Index at 25° C.
vs.
Hours Blown

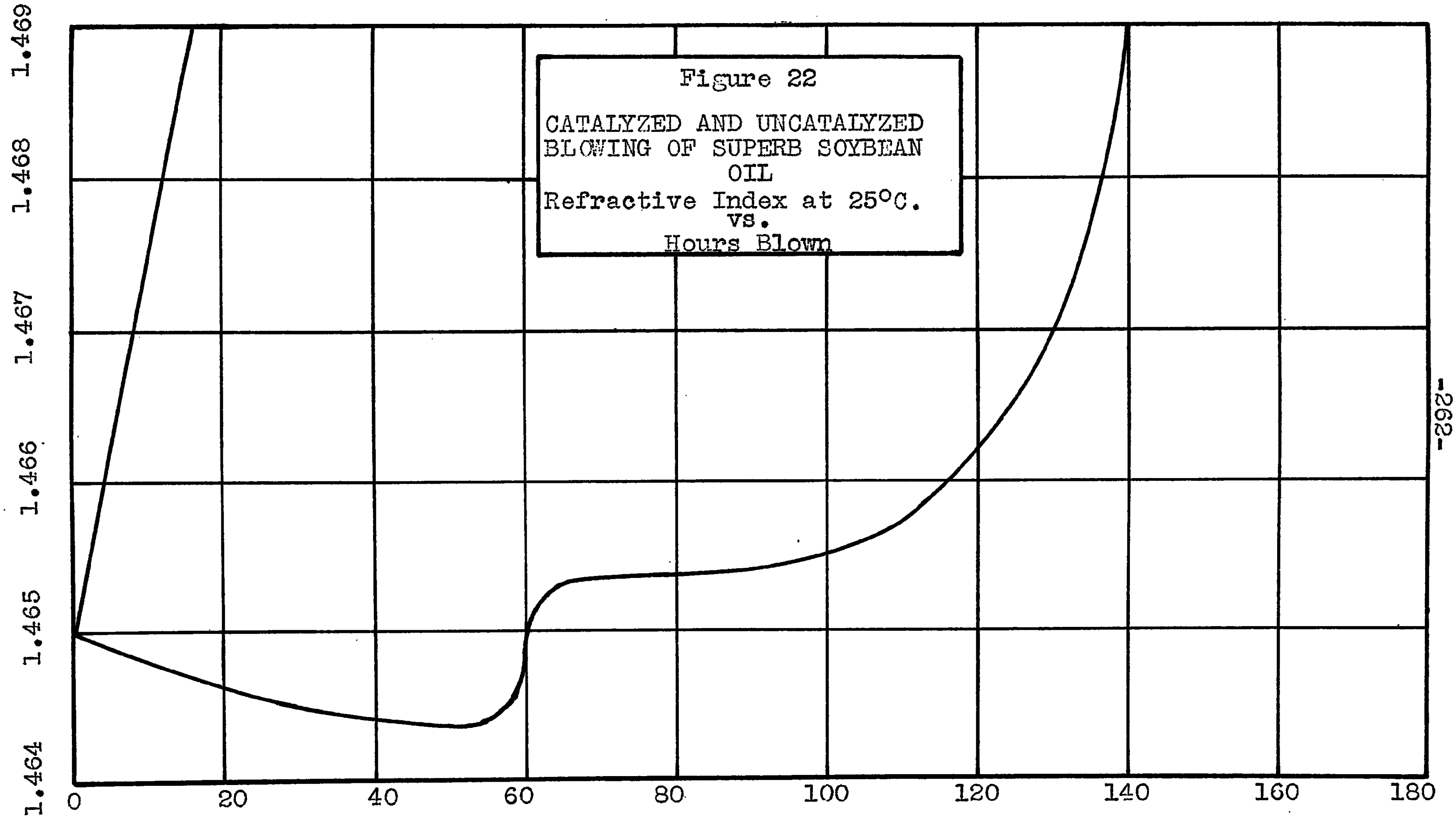


Figure 22

CATALYZED AND UNCATALYZED
BLOWING OF SUPERB SOYBEAN
OIL
Refractive Index at 25°C.
vs.
Hours Blown

TABLE XII.

Comparison of Blowing Times of Various Oil Samples

Oil	Temperature	Catalyst	Induction Period	$\Delta n_D^{25^\circ}/\Delta$time
Superb linseed	40°C.	none	48.5 hrs.	2.6
SH'd linseed	40°	none	25	1.7
Raw linseed	40°	none	25	5.0
Superb soya	40°	none	100	3.3
Non-break perilla	40°	none	75	2.2
Refined menhaden	40°	none	0	1.9
Superb linseed	$40\text{-}50^\circ$	none	11	2.2
Superb linseed	75°	Dry air	7	6.7
Superb linseed	80°	Saturated air	1½	4.0
Superb linseed	25°	0.005%Co	0	1.8
SH'd linseed	45°	0.005%Co+0.0025%Mn	0	8.6
Raw linseed	50°	0.005%Co+0.005%Mn	0	6.4
Superb soya	50°	0.005%Co	0	2.4

In order to study the changes in the various oil properties during the blowing process, a run was made on Superb linseed oil by blowing it at 40°-50° C. until its refractive index had risen 40 points. The data obtained is tabulated in Table XIII. These results are plotted in Figures 23 to 28 inclusive.

Aside from small variations in data, typical induction periods are shown by the changes in refractive index, iodine number, viscosity, molecular weight and specific gravity during the initial blowing of the oil. At the end of this period there is an abrupt and rapid change in these properties. On the other hand, the acid value appears to continuously increase; this may be a key to the mechanism of the blowing process.

TABLE XIII.

Blowing of Superb Linseed Oil

Sample Number	Elapsed Time, Hours	$n_D^{25°}$	Absolute Viscosity	Specific Gravity	Molecular Weight	Bolton Williams I_2 Number	Acid Value
1	0	1.4712	0.443	0.9277	887	160.5	0.33
2	3	1.4712	0.447	0.9279	892	158.2	0.39
3	8	1.4711	0.437	0.9288	909	156.2	0.47
4	12	1.4714	0.502	0.9294	906	158.5	0.58
5	16	1.4718	0.525	0.9323	920	155.2	0.92
6	19	1.4726	0.726	0.9390	988	146.4	1.45
7	21	1.4732	0.828	0.9432	1009	142.6	1.74
8	22.5	1.4736	0.988	0.9459	1042	139.8	1.85
9	24	1.4741	1.042	0.9490	1073	136.7	2.04
10	26	1.4747	1.330	0.9544	1106	132.9	2.35
11*	28.25	1.4752	1.727	0.9571	1172	126.7	2.59

* Resin solubility.

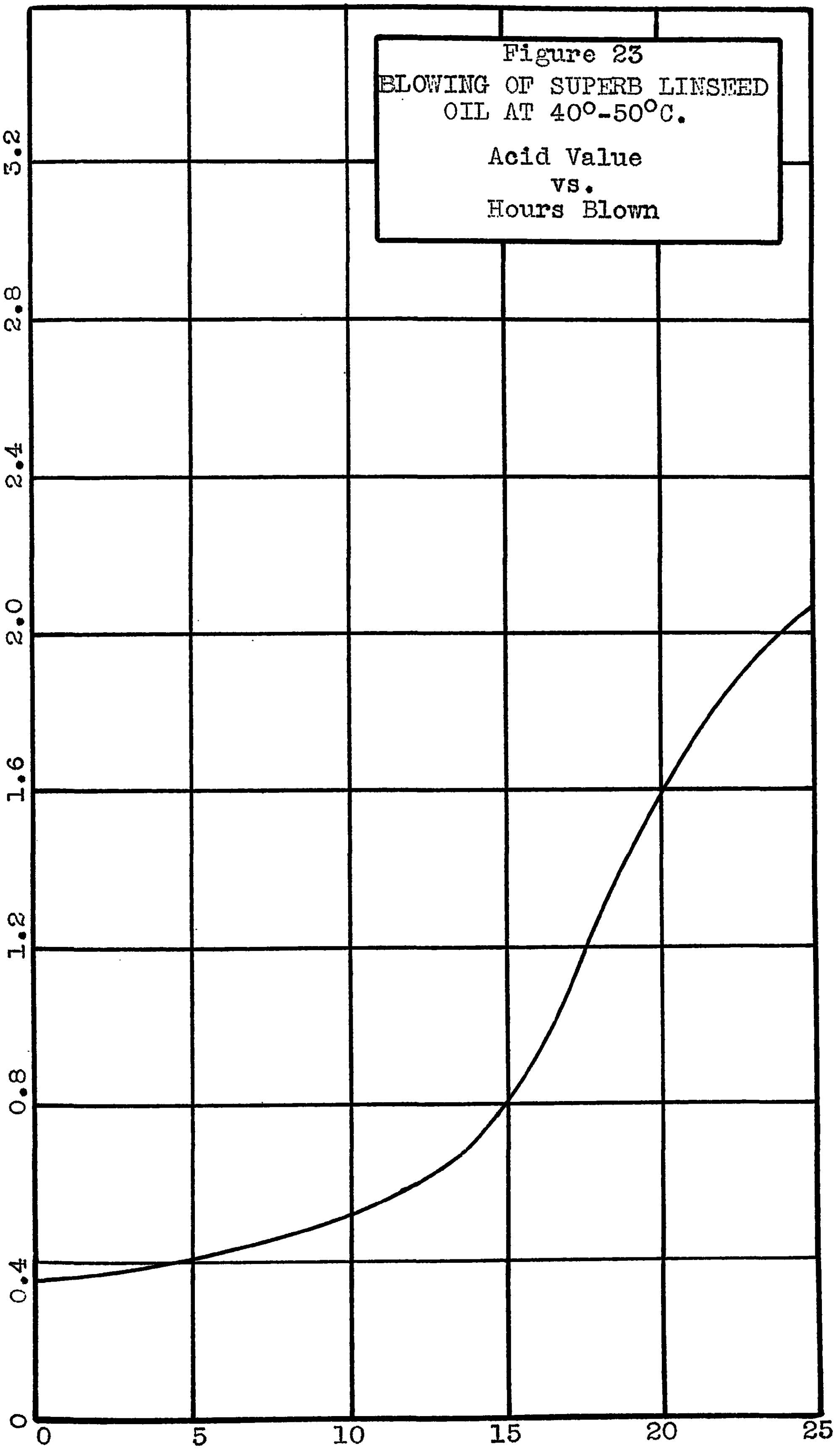


Figure 23
BLOWING OF SUPERB LINSEED OIL AT 40°-50°C.

Acid Value
vs.
Hours Blown

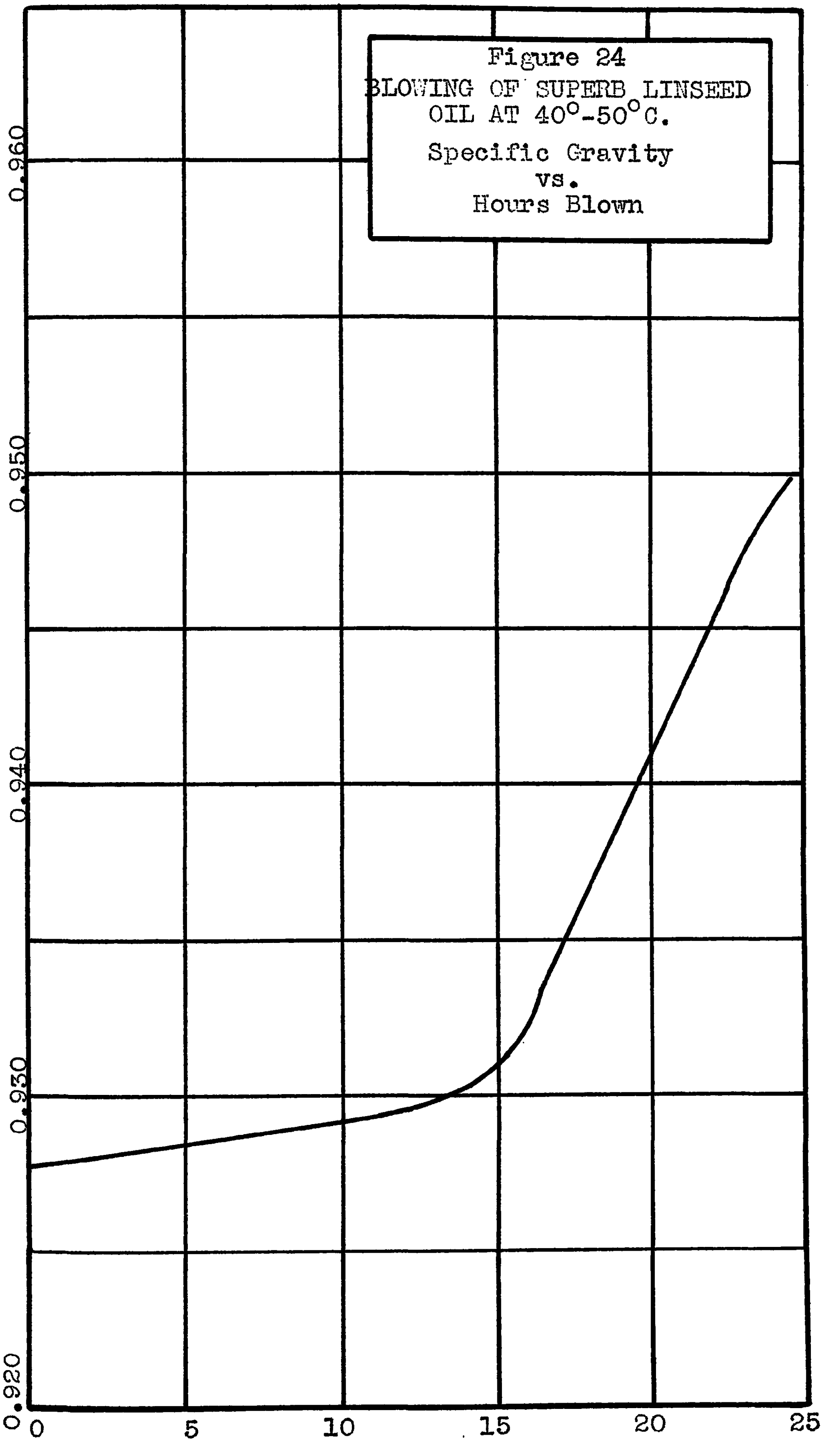


Figure 24
BLOWING OF SUPERB LINSEED OIL AT 40°-50°C.

Specific Gravity
vs.
Hours Blown

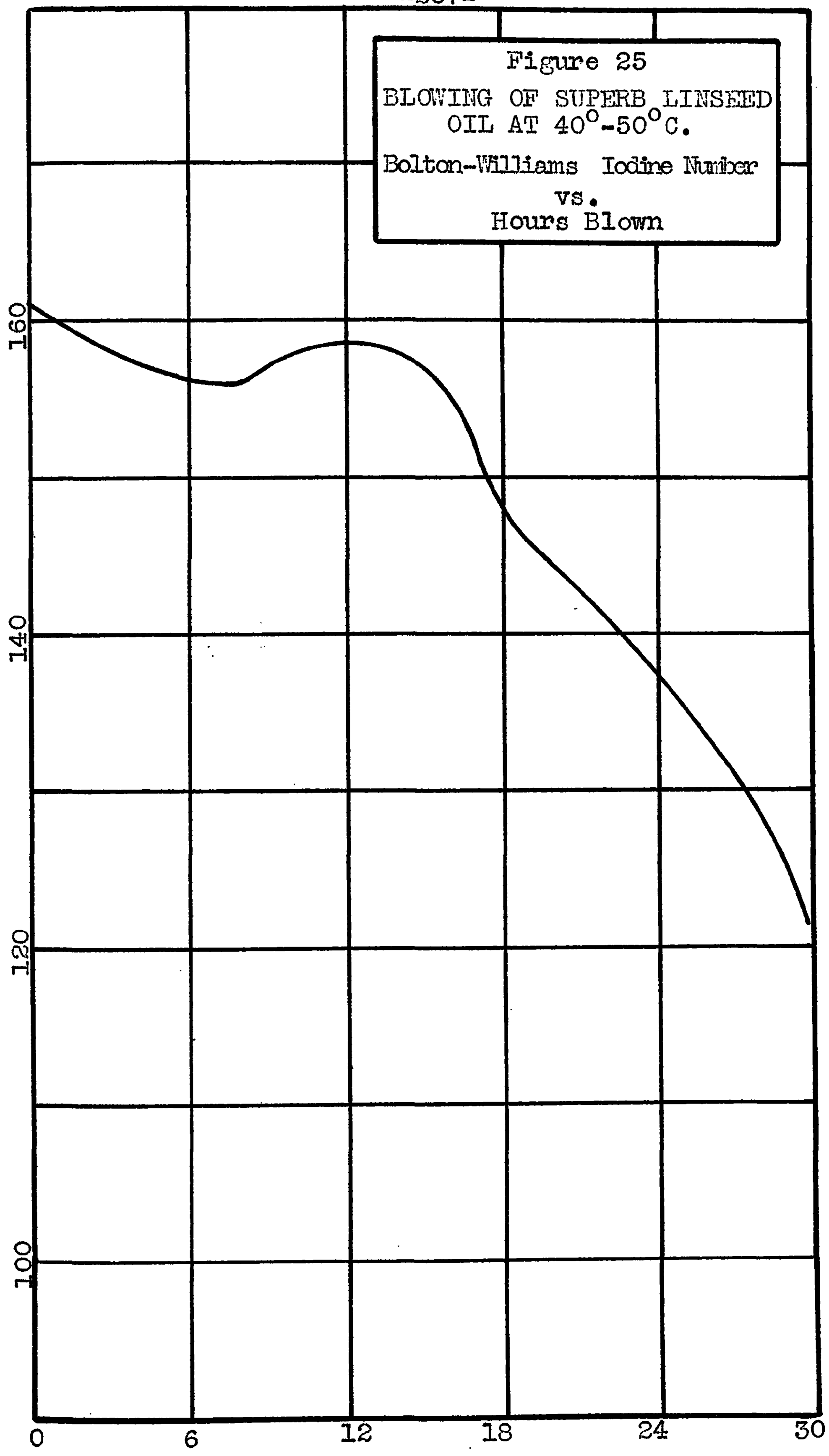


Figure 25

BLOWING OF SUPERB LINSEED OIL AT 40°-50°C.

Bolton-Williams Iodine Number
vs.
Hours Blown

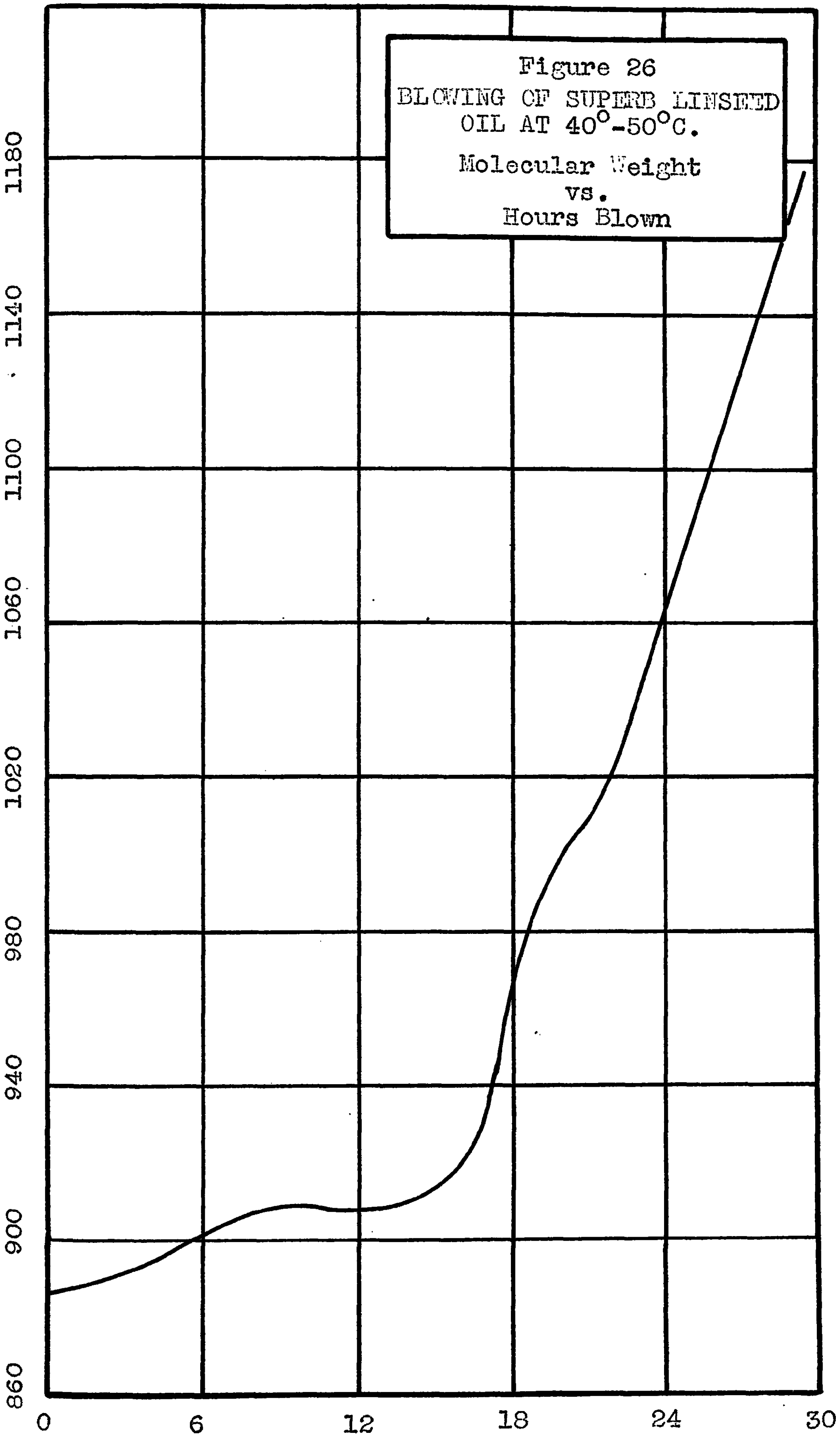


Figure 26
BLOWING OF SUPERB LINSEED OIL AT 40°-50°C.
Molecular Weight
vs.
Hours Blown
1180
1140
1100
1060
1020
980
940
900
860
0
6
12
18
24
30

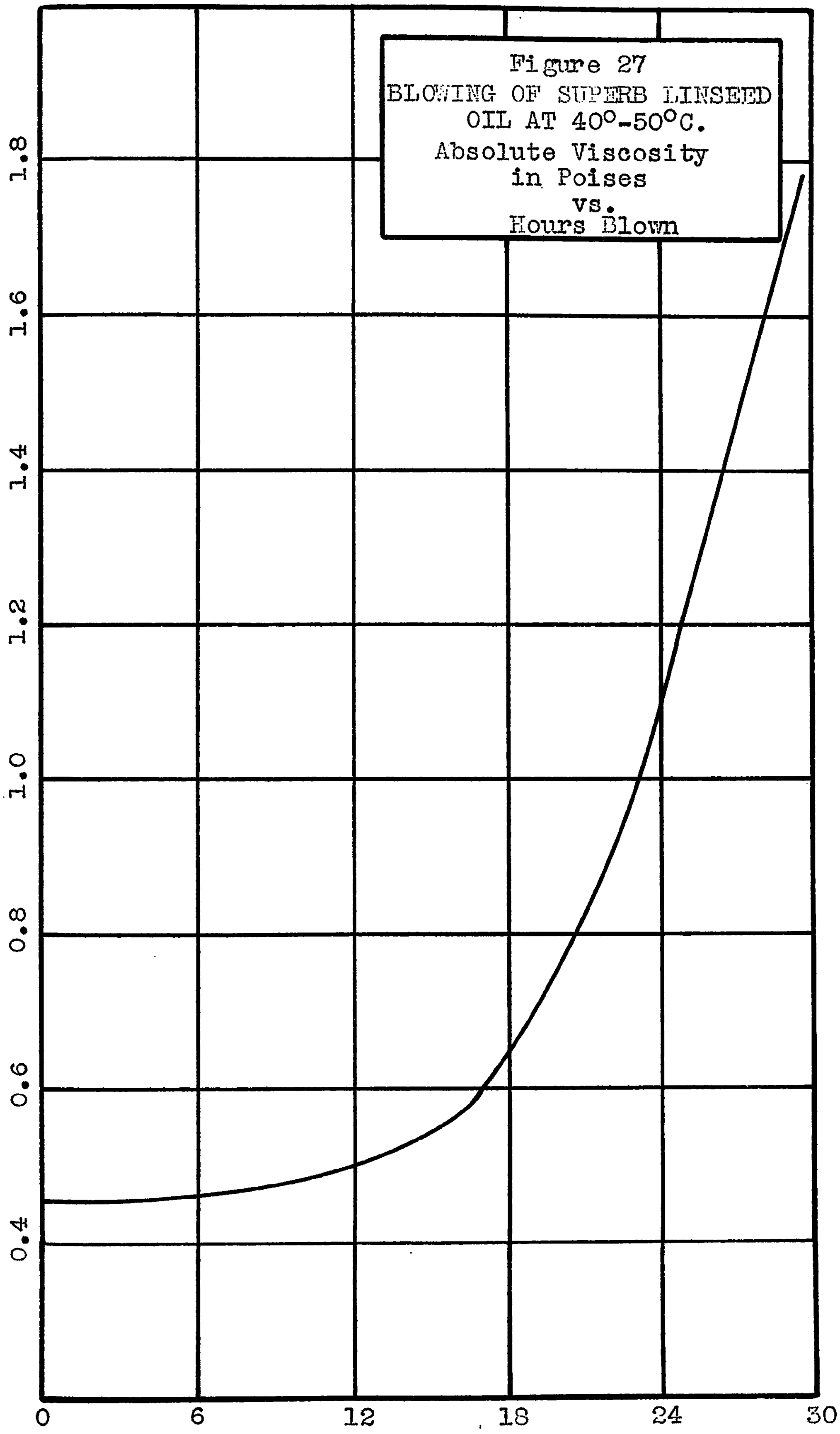


Figure 27
BLOWING OF SUPERB LINSEED
OIL AT 40°-50°C.
Absolute Viscosity
in Poises
vs.
Hours Blown

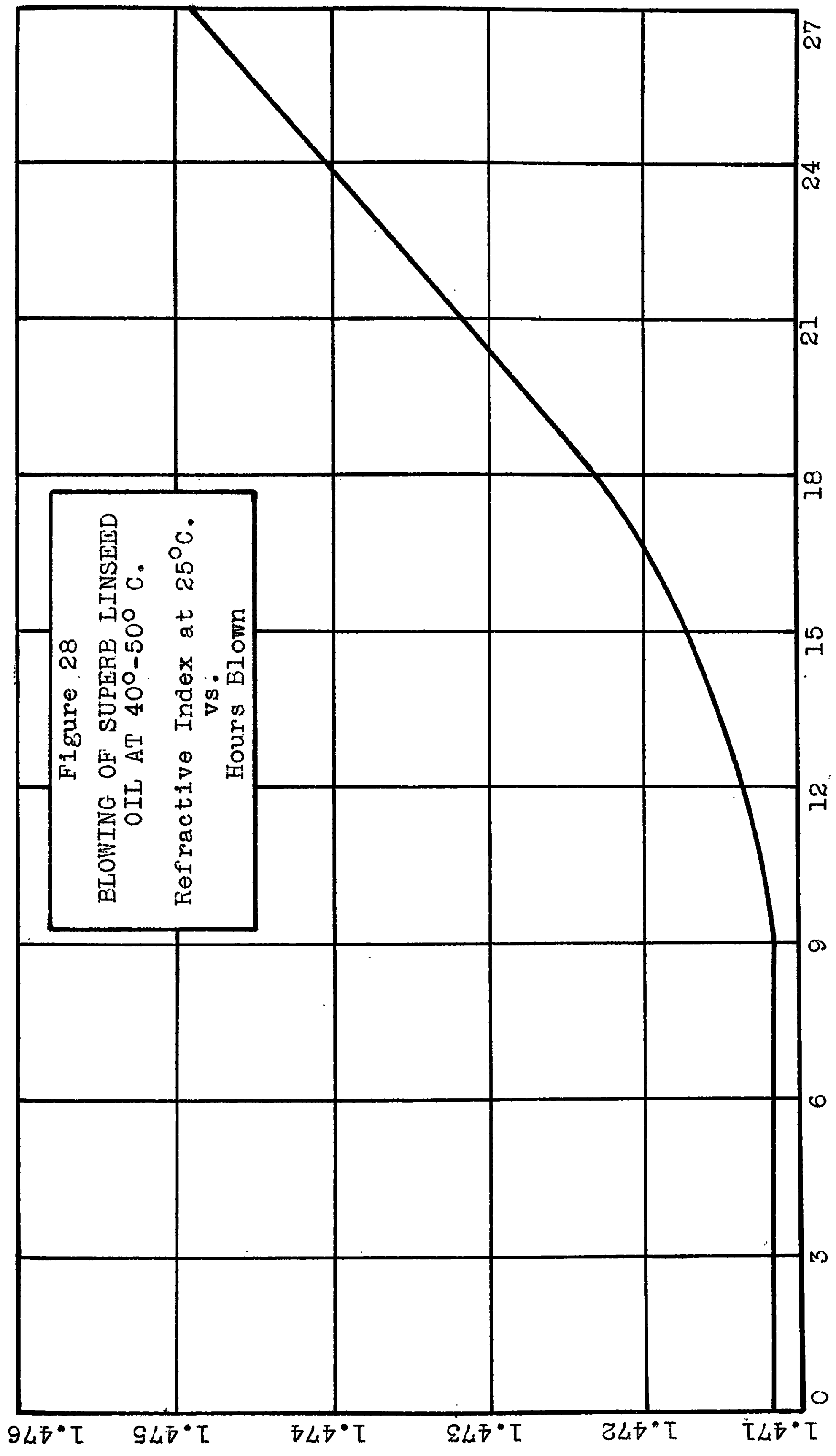


Figure 28
BLOWING OF SUPERB LINSEED OIL AT 40°-50° C.

Refractive Index at 25°C.
vs.
Hours Blown

Production Of Pressure Oxidized Oils

(1) Calibration - Before test runs could be made, it was necessary to check the apparatus for leakage and to correlate the thermocouple reading with the true temperature of the oil sample.

Leakage tests were run from time to time and either corrections to the data were indicated or the source of the leak was detected and repaired.

The thermocouple was inserted in a metal well which was separated from the inner atmosphere of the liner by an air film and another metal film. Consequently, the thermocouple had a pronounced lag in its temperature recordings. Two systems, neither of which were entirely satisfactory, were used to determine the true correlation.

In the first attempt, the liner was removed, filled with 1.5 liters of linseed oil, and heated over the flames of two Bunsen burners. During this heating the thermocouple was connected as usual and readings were taken, which were correlated with the readings of a mercury thermometer immersed in the oil at the opposite end of the liner. The results of these tests are shown in Table XIV. Although these results are erratic, a definite thermocouple lag is indicated, both on cooling and on heating the oil. The lag during the rapid heating of the oil is quite appreciable and should be correlated with all test data.

TABLE XIV

Thermocouple Calibration

Thermocouple Temperature	Thermometer Temperature	Δt°	Time Minutes
114°F.	149°F.	-35	10
121	165	-44	18
135	177	-42	24
139	178	-39	27
141	190	-49	30
150	195	-45	33
154	204	-50	37
166	201	-35	40
102	176	-74	
125	183	-58	
131	172	-41	
141	181	-40	
147	183	-36	
158	201	-43	
168	194	-26	
181	207	-26	
176	185	-9	
174	182	-8	
164	171	-7	
159	160	-1	
150	154	-4	
143	147	-4	
140	138	2	
137	128	9	
131	123	8	
125	118	7	
122	113	9	
120	107	10	

After a number of test runs had been made, a definite heating schedule was standardized. Experience had shown that temperatures in the range of 130°-160°F. were both safe and practical for oxidation work under pressure. Accordingly, a new correlation of the thermocouple was made on the basis of the pressure increase in the autoclave when filled with N_2 gas and heated. This correlation applies with fair accuracy to all runs made at moderate pressures and temperatures; that is, runs which last less than two hours. Most of the subsequent work will be seen to be of this nature. The data from this test is shown in Table XV and plotted in Figure 29.

TABLE XV

Thermocouple Calibration

Time Minutes	Gage Pressure	Thermocouple Temperature	True Temp.	Δt^o	Heating Schedule
0	88.3#/in^2	76°F.	76°F.	0	High heat on
15	91	76	93	-17	
22	94.5	92	113	-21	
25	95.5	94	120	-26	Medium Heat
30	98	104	135	-31	
40	99	110	142	-32	Low Heat
45	100.5	118	150	-32	
50	101	120	153	-33	Heat Off
55	101-	126	153	-27	
60	100.5	126	150	-24	
65	100.5	127	150	-23	
75	100.5	127	150	-23	
105	98.5	126	144	-18	

These results show that the thermocouple lags between 20 and 30 degrees behind the true oil tempera-

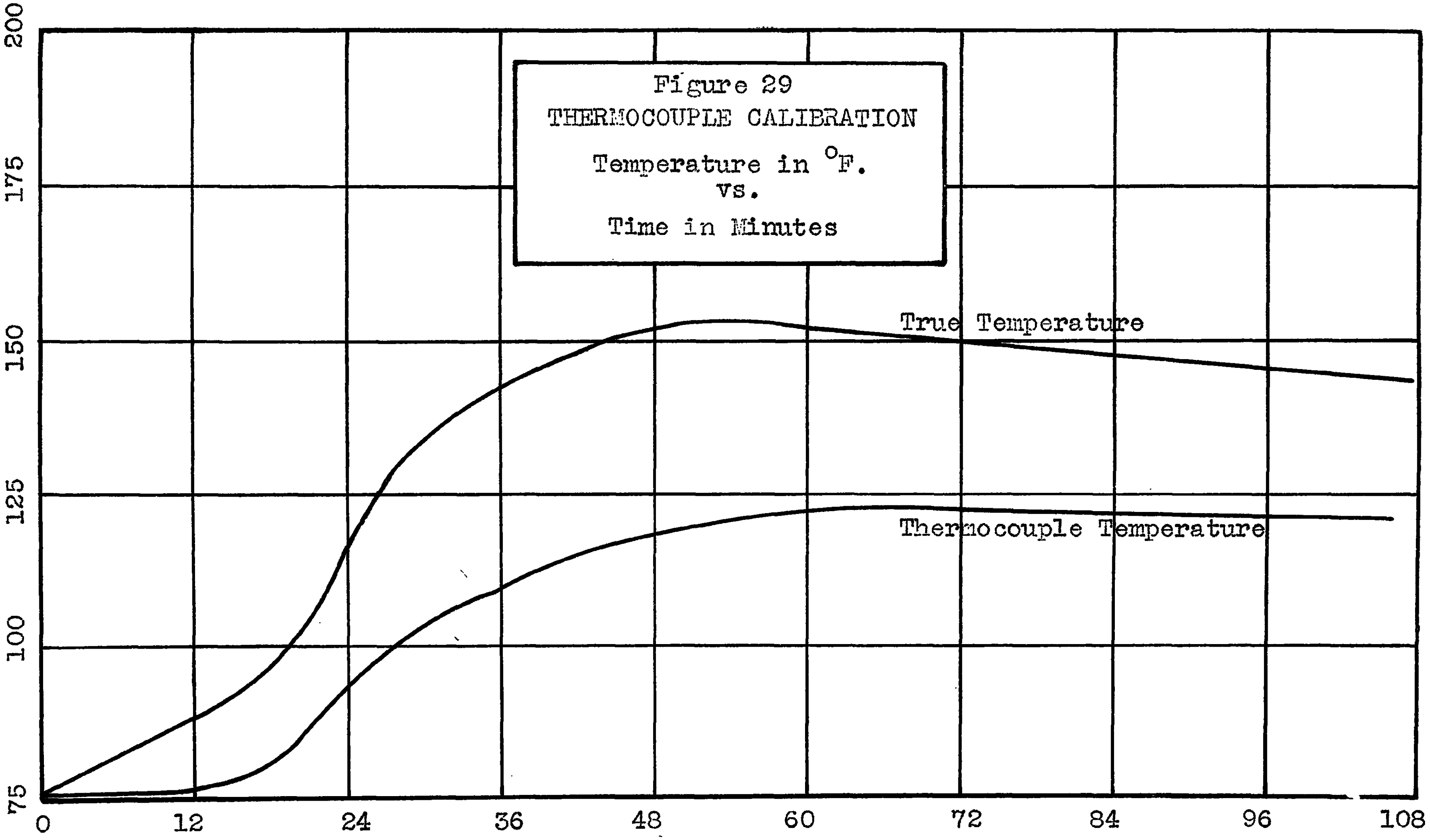


Figure 29
THERMOCOUPLE CALIBRATION
Temperature in °F.
vs.
Time in Minutes

ture. Consequently, the observed temperatures as recorded for the various test runs, should be modified by the appropriate amounts in each case.

(2) Effect of Pressure - In initiating this work on the pressure oxidation of drying oils, 100 grams of Superb linseed oil were taken as a standard sample. The first few runs were made at relatively high pressures (1500 #/in^2) and at temperatures varying from 80-180°F. These results were either definitely negative or uncontrollably positive; they may be summarized as follows:

TABLE XVI

Run No.	Hrs. Time	Pressure (#/in^2) Initial	Pressure (#/in^2) Maximum	Temperature (°F) Average	Temperature (°F) Maximum	Results
1	2-2/3	1450	1450	80°	80°	Negative
2	15	1500	1500	73°	73°	Negative
4	5½	1350	>6000	150°	>1000°	Explosion

A second series of runs were made at intermediate pressures (450-800 #/in^2). The results were quite variable and difficult to control; they are summarized in the following table:

TABLE XVII

Run No.	Hrs. Time	Pressure (#/in^2) Initial	Pressure (#/in^2) Maximum	Temperature (°F) Average	Temperature (°F) Maximum	Results
8	4	700	700	130°	135°	Negative
10	½	575	>1000	180°	<700°	Explosion
13	7	400	400	130°	145°	Index rise
14	6	780	780	140°	155°	Gel formed

In run #10, the autoclave was preheated to 180°F. before pressure was applied. In less than five minutes uncontrolled oxidation occurred. The residue from the oil consisted of a soft, thick, black mud and a number of brittle, hard, metallic particles, probably graphitic materials.

In run #13, the main body of oil rose 8 points in index while a small residium, which overflowed into the outer chamber of the autoclave, showed an increase of 56 points in refractive index. The overheating of this residual oil evidently caused a definite oxidation.

Run #14 is the most interesting of all. Oxidation had produced a clear, yellow gel which was somewhat oily and extremely tenacious. When this gel was heated, it foamed violently and exothermically above 110°C. and fumes irritating to the eyes were produced. The action of solvents on this gel was investigated in some detail. The results obtained were as follows:

1. <u>Benzene</u> - The gel absorbs the solvent and fuses to a brownish mass when heated to 200° C. The mass sets to a clear, sticky film.

2. <u>Carbon tetrachloride</u> - A similar reaction to the above, but the gel sets to a clear, wrinkled skin.

3. <u>Ethyl alcohol (95%)</u> - Some slight solu-

bility is found near the boiling point of the alcohol.

4. Skellysolve E - A cloudy solution is formed at 80°C.

5. Methyl cellosolve - At 120°C., a reaction or solution sets in, irritating fumes are produced, and a clear, yellow solution is formed.

6. Skellysolve C - Some solubility is found at 85°C.; a cloudy solution is formed.

7. Light naphtha - The gel is only softened.

8. n-Butanol - A reaction occurs at 100° C., resulting in a clear, light colored solution.

9. Butyl acetate - A good solution is obtained at 105°C.

10. Butyl proprionate - The gel begins to dissolve at 80°C. and is completely in solution at 100°C.

11. Diethylene glycol - The gel softens at 80°C., is slightly dissolved at 110°C. at which point a reaction occurs and raises the temperature to 125°C. The final solution is cloudy and deeply yellow.

12. Essotex - A brownish, partial solution is produced at 110° C.

13. Butyl acetylricinoleate - Solution begins at 70°C. but is still incomplete at 100°C.

14. Diethyl carbinol - Solution begins at

70°C. and is complete and clear at 100°C.

15. Diamyl ether - Complete solution is found at 100°C.

16. Butyl stearate - The gel is only slightly soluble.

17. 2-Ethyl Hexyl Acetate - A clear solution is formed at 110°C.

18. Cellosolve Acetate - A clear solution is formed at 110°C.

19. Diacetone - At 110°C., a clear, yellow solution is formed.

20. Methyl lactate - The gel is partially soluble at 110°C.

21. Secondary butyl alcohol - The gel softens at 40°C. and is partially dissolved at the boiling point of the solvent.

A solution of this gel was made in butanol, but the film produced on an amalgamated aluminum plate was too thin for test purposes.

As a result of these preliminary tests, it was decided to work at low oxygen pressures and determine the effects of temperature, pressure, concentration and catalysts on the production of an index oil. The primary aim, of course, was to develop the best process for index oil production. The results on these runs are summarized in Table XVIII and are discussed in more detail under the respective subheadings, which refer to the subscripts on the run designation. Representative data will be given in each of these subsections.

<u>Key To Table XVIII</u>:

P_g = initial gage pressure corrected to 100°F. (#/in^2)

P_m = maximum gage pressure corrected to 100°F. (#/in^2)

ΔP = drop in pressure, initial to final (#/in^2)

t_a = average temperature (°F.)

t_m = maximum temperature (°F.)

T_g = time starting from the application of gas pressure (hrs:min)

T_{100} = time starting from temperature of 100°F. (hrs:min)

W = quantity of oil (grams)

Δn - refractive index at 25°C. (rise)

Δw = per cent oxygen absorption calculated from ΔP

R_s = resin solubility

t_r = temperature of resin solubility (°C.)

t_e = temperature of exothermic reaction when oil is heated to 200°C. (°C.)

C = color of oil (comparative)

C_x = color of oil after heating to 200°C.

G = Gardner-Holt bubble tube viscosity

r = Absolute viscosity in centipoises

TABLE XVIII

Run No.	Type Oil	Gas	Catalyst[†]	W	P_g	P_m	t_a	t_m
100	Superb linseed	---	----	----	-----	-----	---	----
101	Tung	---	----	----	-----	-----	---	----
102	SH'd linseed	---	----	----	-----	-----	---	----
103	Raw linseed	---	----	----	-----	-----	---	----
104	perilla	---	----	----	-----	-----	---	----
105	soybean	---	----	----	-----	-----	---	----
106	menhaden	---	----	----	-----	-----	---	----
107	linoleic-oleic[x]	---	----	----	-----	-----	---	----
108	40 pt.linseed[o]	---	----	----	-----	-----	---	----
20a	Superb linseed	O_2	None	100	38	41	142	154
21a	" "	"	"	"	55	56	135	155
23a	" "	"	"	"	70	75	139	159
25a	" "	"	"	"	70	77	137	157
24a	" "	"	"	"	85	92	132	171
22b	" "	"	"	"	40	45	150	196
26c	" "	"	"	"	70	74	---	149
27c	" "	"	"	"	70	75	---	160
36c	" "	"	"	"	73	76.5	---	140
37c	" "	"	"	"	74	77	---	168
38c	" "	"	"	"	71.5	86	142	171
39c	" "	"	"	"	71.5	86	---	172
31d	" "	"	Al coil	"	72.5	72.5	110	132
32d	" "	"	Al coil	"	72	73	120	140
33d	" "	"	Al coil	"	74	75.5	---	135
34d	" "	"	Al coil	"	73.5	75	---	143
35d	" "	"	Al coil	"	73	82.5	---	145
17e	" "	"	0.07%Co;0.34%Pb	"	1350	1350	129	150
28e	" "	"	0.005%Co	"	71	71	105	145
29e	" "	"	0.005%Co	"	71	71	109	137
30e	" "	"	0.005%Co	"	72	72	108	130

Run No.	Δn	ΔP	Δw	R_s	t_r	t_e	T_g	T_{100}	C	C_x	G	r
100	---	------	---	No	---	---	-----	-----	5	5	A	50
101	---	------	---	Yes	130	---	-----	-----	11	11	S	500
102	---	------	---	No	---	---	-----	-----	15	15	A-B	57
103	---	------	---	No	---	---	-----	-----	10	10	A-B	57
104	---	------	---	No	---	---	-----	-----	6	6	B	65
105	---	------	---	No	---	---	-----	-----	3	3	B	65
106	---	------	---	No	---	---	-----	-----	12	12	A	50
107	---	------	---	Yes	50	---	-----	-----	12	12	H	200
108	40	------	---	Yes	100	----	-----	-----	12	13	L	300
20a	44	20	5.8	Yes	100	130	5:00	4:50	8	--	L	300
21a	29	22	6.4	Yes	60	140	4:00	3:20	7	10	F	140
23a	40	24.5	7.1	Yes	60	115	3:30	2:45	7	15	I	225
25a	39	16	4.7	Yes	60	130	2:45	2:30	6	12	H	200
24a	45	28.5	8.3	Yes	100	115	2:30	1:50	8	15	P-Q	417
22b	35	21	6.1	Yes	60	---	3:00	2:30	10	13	L-M	310
26c	2	7	---	No	---	---	2:30	2:00	5	6-	A	50
27c	0	10.5	---	No	---	---	3:00	2:10	6-	--	A	50
36c	1	7	---	No	---	---	3:00	2:40	--	--	A	50
37c	3	20	---	No	---	---	4:30	4:00	--	--	A	50
38c	2	-1	---	No	---	---	5:10	4:35	--	--	A	50
39c	2	1	---	No	---	---	5:30	5:15	--	--	A	50
31d	11	11	3.2	Borderline	---	---	1:30	1:00	5	8	B	65
32d	2	9	2.6	No	---	---	2:00	1:30	6	6-	A-B	57
33d	2	11	---	No	---	---	2:20	1:50	--	--	A-B	57
34d	3	13.5	---	No	---	---	2:20	1:50	--	--	A-B	57
35d	0	1.5	---	No	---	---	7:00	6:45	5	5	A-B	57
17e	Gel	230	---	--	---	---	2:30	2:10	--	--	---	--
28e	50	15.5	4.5	Yes	40	115	2:15	2:00	7	20	L	300
29e	40	13	3.8	Yes	40	110	1:00	0.40	6	20	F-G	152
30e	35	10.5	3.1	Yes	60	105	0.45	0.30	6	15	D	100

Run No.	Type Oil	Gas	Catalyst†	W	P_g	P_m	t_a	t_m
40e	Superb linseed	O_2	0.005%Co	100	72	73.5	113	147
41e	" "	"	0.005%Co	"	73	74.5	103	130
45f	" "	"	None	"	-----	-----	122	133
46f	" "	"	"	"	73.5	84.5	134	157
47f	" "	"	"	"	72	79	131	169
43f	" "	"	"	"	72	72	---	152
44f	" "	"	0.005%Co	"	73	73	135	138
50g	" "	"	0.005%Co	"	88.5	89	100	130
51g	" "	"	0.005%Co	"	102.5	102.5	122	128
52g	" "	"	0.005%Co	"	30.5	31	125	137
61h	" "	"	0.001%Co	"	87	94.5	113	142
48i	" "	"	0.005%Co Al coil	"	75	77.5	97	124
53i	" "	"	0.005%Mn	"	87.5	97.5	119	146
55i	" "	"	0.1%Pb	"	89	94	111	135
56i	" "	"	0.005%Fe	"	83.5	85.5	128	136
54i	" "	"	0.005%Co;0.0025%Mn	"	87.5	87.5	95	114
49i	" "	"	0.05%CH_3COOH	"	72.5	84.5	141	171
79i	" "	"	0.05%KOH;0.2%H_2O	"	87	91.5	138	151
76i	" "	"	0.1% benzoyl peroxide	"	85.5	89.5	126	139
77i	" "	"	0.1% BP in acetone	"	87.5	95	126	138
74i	" "	"	0.005%Co;0.0025%Mn;0.05% HAc	"	86	90.5	121	151
80i	" "	"	0.005%Co;0.0025%Mn;0.1% BP	"	85.5	85.5	110	128
78i	" "	"	0.2%HAc;0.1%BP	"	85.5	85.5	130	141
81i	" "	"	0.005%Co;0.0025%Mn 0.05%HAc;0.1%BP	"	86.5	88.5	112	134

Run No.	Δn	ΔP	Δw	R_s	t_r	t_e	T_g	T_{100}	C	C_x	G	r
40e	53	8	2.3	Yes	60	---	1:05	0:40	8	20	N	340
41e	40	2.5	0.7	Yes	50	90	0.50	0.30	6	--	F	140
45f	5	---	---	---	--	---	8:30	----	-	--	-	---
46f	56	18.5	---	Yes	50	---	2:30	2:10	7	--	S	500
47f	55	13	---	Yes	50	100	1:30	1:10	8	--	S	500
43f	3	---	---	No	--	---	2:50	2:40	5-6	--	A-B	57
44f	37	13	3.8	Yes	50	---	0.30	----	6	15	F-G	152
50g	38	5	1.5	Yes	--	120	0:45	0:20	7	15	G	165
51g	28	7	2.0	Yes	--	110	0:15	0:15	6	13	D-E	112
52g	26	5.5	1.6	Yes	150	120	0.45	0.50	5-6	10	D	100
61h	32	5	1.5	Yes	--	115	1:05	0:42	6	12	F	140
48i	34	2	0.6	Yes	40	100	0:50	0:18	6	15	F	140
53i	8	0	---	---	--	---	1:15	0:55	5	--	B	65
55i	16	3	0.9	Yes	60	135	0:55	0:35	3	8	B	65
56i	2	4	1.2	No	--	---	2:10	2:15	-	--	-	---
54i	29	2.5	0.7	Yes	60	120	0:35	0:10	5	12	D	100
49i	34	6	1.7	Yes	40	125	4:20	3:55	7	12	D	100
79i	42	17	---	Yes	--	105	5:00	4:50	10	25	J-K	262
76i	0	0	---	No	--	---	2:30	2:05	3	5	A	50
77i	0	---	---	No	--	---	2:25	2:00	3	5	A	50
74i	49	7.5	2.2	Yes	--	---	0:55	0:45	8	25	M	320
80i	37	8	2.3	Yes	--	120	0:45	0:35	5	17	F	140
78i	2	0	---	No	--	---	3:50	3:30	3	0-	A-B	57
81i	32	6.5	1.9	Yes	--	120	0:50	0:35	5	15	E	125

Run No.	Type Oil	Gas	Catalyst†	W	P_g	P_m	t_a	t_m
81i	Superb linseed	O_2	0.005%Co;0.0025%Mn 0.05%HAc;0.1%BP	100	86.5	88.5	112	134
57k	" "	"	0.005%Co Al coil	1200	82.5	82.5	128	153
58k	" "	"	0.005%Co;0.0025%Mn	"	115	115	137	158
59k	" "	"	0.005%Co;0.0025%Mn	"	194	194	149	179
60k	" "	"	0.005%Co;0.0025%Mn	"	216	216	144	178
62k	" "	"	0.00017%Co;0.0006%Mn 0.0031%Pb	"	209	209	149	175
63m	" "	Air	0.001%Co	100	305	326.5	----	150
66m	" "	"	0.005%Co;0.0025%Mn	"	368	389	139	154
67p	" "	"	0.005%Co;0.0025%Mn;0.05%Pb	1200	374	374	142	150
68p	" "	"	0.005%Co;0.0025%Mn	"	1230	1250	130	134
69p	" "	"	0.005%Co;0.0025%Mn	"	1485	1510	143	155
64r	" soybean	O_2	0.005%Co;0.0025%Mn	100	86	92	119	149
71r	perilla	"	0.005%Co;0.0025%Mn	"	86	90.5	116	148
75r	menhaden	"	0.005%Co;0.0025%Mn	"	87.5	88	117	138
70r	raw linseed	"	0.005%Co;0.0025%Mn	"	87	90	116	138
72r	SH'd linseed	"	0.005%Co;0.0025%Mn	"	88	96.5	112	133
73r	linoleic-oleic^{x}	"	0.005%Co;0.0025%Mn	"	87.5	96.5	108	135
82t	Superb linseed	N_2	0.05%HAc	"	1060	1111	155	166
83t	Superb linseed	"	0.05%HAc;0.1%BP	"	953	990	155	169

Run No.	Δn	ΔP	Δw	R_s	t_r	t_e	T_g	T_{100}	C	C_x	G	r
57k	16	69	1.0	Yes	80	140	1:00	0:50	-	10	-	---
58k	24	106	1.6	Yes	--	---	1:30	1:20	-	--	-	---
59k	34	178	2.6	Yes	--	---	1:40	1:25	-	--	-	---
60k	40	208	3.1	Yes	--	140	1:30	1:10	7	15	I	230
62k	31	209	3.1	Yes	--	---	1:40	1:35	6	13	H	200
63m	0	12	---	No	--	---	1:45	1:15	-	--	-	---
66m	45	22	3.2	Yes	--	---	1:45	1:45	5-6	--	I	225
67p	14	70	1.0	Borderline	170	---	4:00	4:00	9	--	B	57
68p	33	235	3.4	Yes	--	---	2:00	2:00	5	--	E	125
69p	43	195	2.9	Yes	--	---	1:15	1:15	6	15	H	200
64r	46	8	2.3	Yes	60	110	1:10	0:50	3	12	I-J	237
71r	44	14	4.1	Yes	60	---	1:15	0:50	8	23	T	550
75r	44	11.5	3.3	Yes	60	95	1:00	0:45	11	50	I	225
70r	36	8	2.3	Yes	--	---	0:50	0:35	10	14	G	165
72r	42	9	2.6	Yes	--	130	1:40	1:10	10	17	I	225
73r	17	6	1.7	Yes	50	---	1:45	1:20	11	--	S	500
82t	3	-	---	No	--	---	7:30	7:30	5	5	A	50
83t	13	-	---	Yes	140	---	7:30	7:30	3	7	B	65

† catalyst code: C_o, M_n, P_b, and F_e are present as naphthenates (Nuodex);
HAc is glacial acetic acid; BP is benzoyl peroxide

x Linoleic-oleic mixture is a 1:1 acid mixture (I_2 number = 132.7)

o 40 point linseed is an percolator blown sample used for comparison

Series (a): In these runs the pressure of pure oxygen was varied within narrow limits to determine optimum conditions. A check run was made at 70# pressure to determine the reproducibility of the method.

The complete working data of run 21a is shown in Table XIX as a typical run of this series.

TABLE XIX

100g. Superb linseed - no catalyst - oxygen gas

Time	Heat	Rheostats	P_g	P'_g	t^o
0:00	High	0-0	52	54	80
0:30	Medium	"	54.5	55	95
0:45	"	"	55.5	55	105
1:00	"	"	56	54.5	120
1:15	"	"	56	53.5	128
1:30	"	"	56	52.5	135
1:45	Low	"	56.5	52.5	145
2:00	"	"	56	51.5	149
2:15	"	"	54.5	50.5	151
2:30	"	"	53.5	48.5	153
2:45	"	"	52.5	47.5	154
3:00	"	"	51	46.5	154
3:15	"	"	48	43.5	155
3:30	"	"	44.5	40.5	155
3:45	"	"	40	36.5	155
4:00	Off	Off	36	32.5	155

In all these data tables, the following designations are used:

time = hours:minutes

heat = control switch readings

P_g = the actual gage pressure in $\#/in^2$

P'_g = the gage pressure in $\#/in^2$ corrected to 100^oF.

t^o = the temperature in ^oF.

The rate curves for these runs are plotted in Figure 30. In all cases a definite induction period is indicated, but its quantitative significance is slight in these runs. The autoclave liner was not perfectly cleaned of some cobalt and lead drier from run 17e; consequently, all these runs, and particularly the early ones, are influenced to some extent by traces of catalyst. As will be shown in subsection (f), the oxidation reaction does not proceed when no catalyst is present. Therefore, these runs should be considered as catalyzed tests.

A comparison of the slopes of these rate curves does show some interesting results. As the pressure increases the rate of oxidation also increases and would finally become infinite, at which point an uncontrollable explosion would occur. These results indicate that oxygen pressures over 100 #/in^2 become dangerously active in promoting oil oxidation. In run 24a the temperature rose to a maximum of 171°F. and control was very difficult; higher pressures will cause still more difficulty in controlling the exothermic nature of the oxidation reaction.

The time to produce a 40 point oil is enormously decreased by increasing pressure. Oxidation at 40# requires nearly 5 hours, whereas at 85#, less than 2 hours are necessary.

In every case the index oils showed resin solubility, although the more highly indexed oils

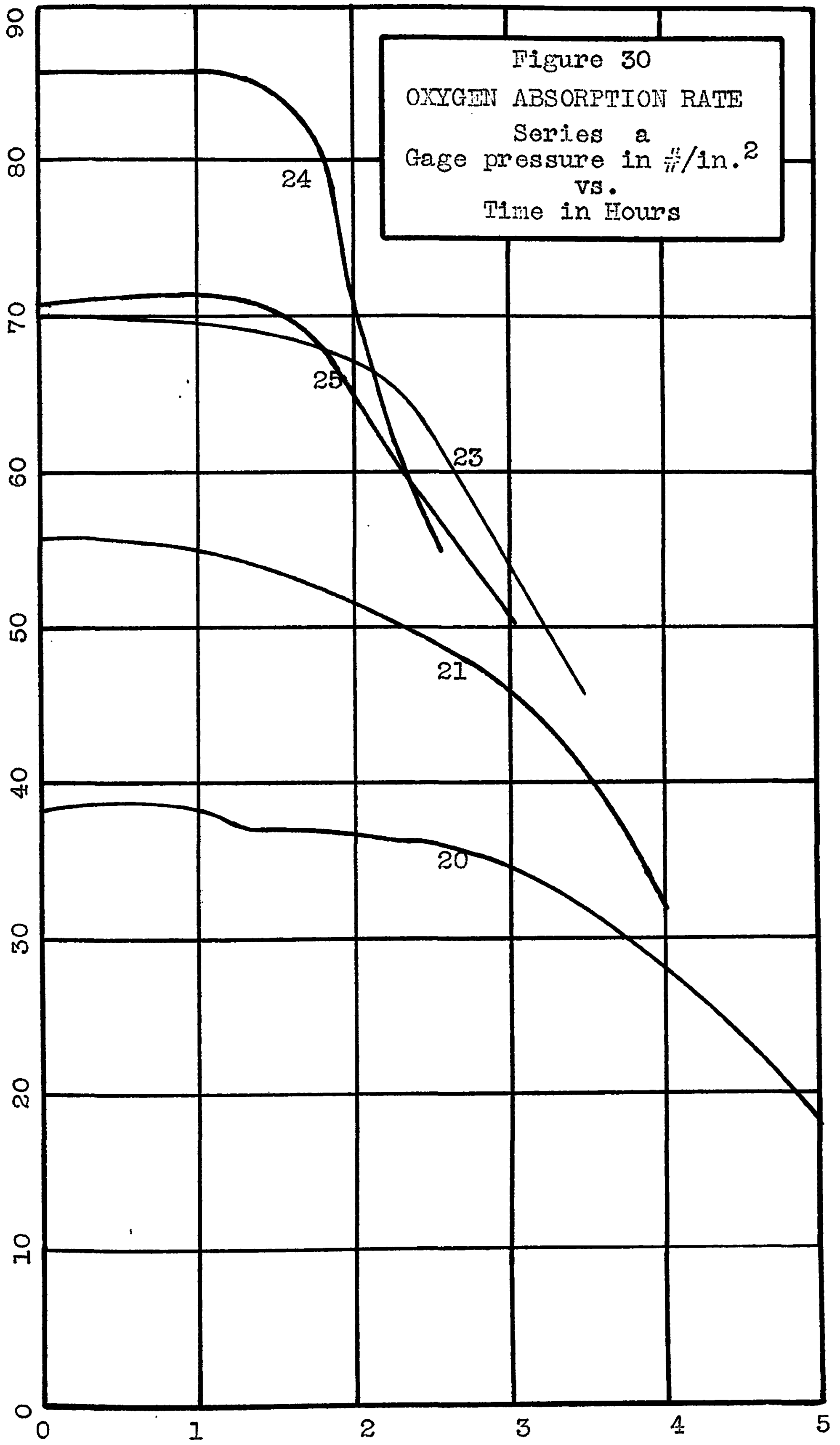


Figure 30
OXYGEN ABSORPTION RATE
Series a
Gage pressure in #/in.^{2}
vs.
Time in Hours

seemed slower in their reaction.

The viscosity and the color after heating appear to depend more on the index and the temperature than on the pressure during the run.

<u>Series (b)</u>: In run 22b, the effect of temperature is clearly demonstrated. Although the pressure was the same as in run 20a, the time of oxidation was reduced from 5 hours to 2½ hours.

As expected, the viscosity and the color of the oil were adversely affected by the increase in temperature.

The oxygen absorption was of the same order of magnitude as in the (a) Series, but, in both series, the quantitative values of this absorption is in error due to variable leakages in the pressure system.

The rate curves of runs 20a and 22b are reproduced in Figure 31 for comparison.

<u>Series (c):</u> These runs were made at approximately the same pressure (70# gage) but the temperature and time were varied when it became apparent that oxidation was not occurring.

Although the time was increased to over five hours, no significant changes occurred in refractive index, viscosity or color. Furthermore, none of the oils showed resin solubility. When the system was leak-tight, no oxygen absorption took place.

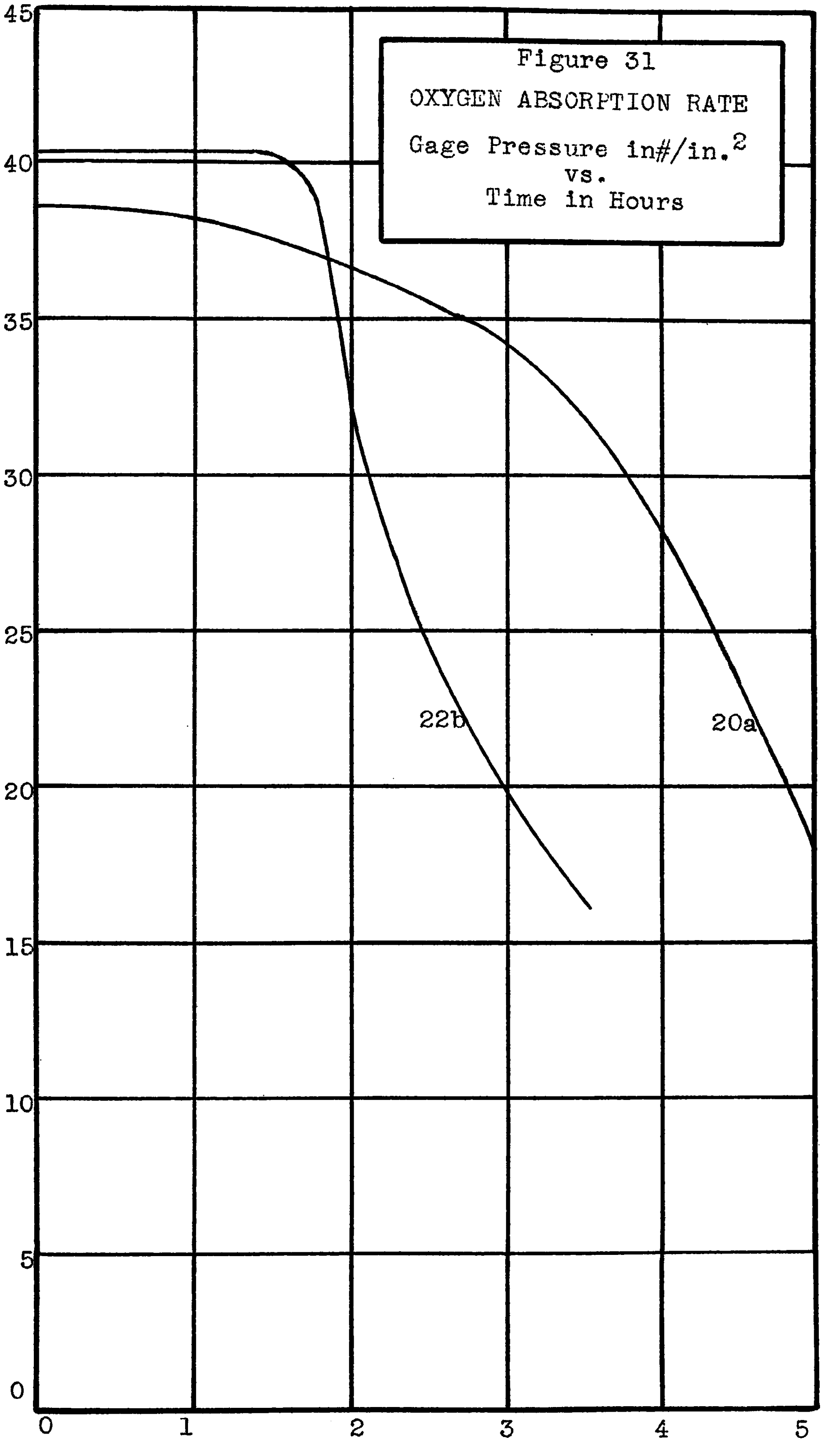


Figure 31
OXYGEN ABSORPTION RATE
Gage Pressure in#/in.^{2}
vs.
Time in Hours
45
40
35
30
25
20
15
10
5
0
0
1
2
3
4
5
22b
20a

This series indicates that an oil under pressure in a leak-tight autoclave does not oxidize at low pressures and temperatures when no catalyst is present and the time of oxidation is under six hours.

Series (d): Since the autoclave design does not cause much agitation with small samples, a spiral-wound aluminum coil was suspended inside the liner in such a way that it was free to rotate and to slide lengthwise. This series of runs were made at relatively constant temperature and pressure to determine if induced foaming would promote the oxidation of the oil.

In the run 31d, a partially oxidized oil was produced. Its index had increased 11 points; it apparently had resin solubility, but later examination proved this false. Its color and viscosity had slightly increased. However, this particular run was thrown out because of catalyst contamination from the previous run, 30e.

In runs 32d to 35d, the autoclave was free from catalyst. As in the (c) series, no index oil was produced, although the time of oxidation was increased to seven hours in one case.

Series (e): In this series, definite, controllable production of indexed oils was accomplished for the first time. The lead to this control came from a catalyzed high pressure run, 17e. In this run, a dark colored, tacky and resilient gel was formed. Although the pressure and temperature were both high, no explosion occurred, and the reaction proceeded smoothly.

Subsequent runs were made at low pressures (70# gage) using 0.005% Co (as Nuodex) catalyst. Data for a typical run of this series (29e) is reproduced in Table XX.

TABLE XX

100g. Superb linseed oil - 0.005%Co catalyst - oxygen gas

Time	Heat	Pg	P'g	t°	Remarks
----	High	----	----	73	Heat on
----	High	----	----	---	O_2 going in
0:00	High	68	71.5	75	Autoclave rocking
0:15	High	69	70.5	90	
0:30	Low	68.5	67.5	110	
0:45	Off	65	61.5	130	
1:00	Off	60	56.5	137	Pressure released

The rate curves for this series are plotted in Figure 32. Since the experimental conditions are similar in every case, no great differences in rate should be experienced. However, the pressure system showed variable leakage conditions which prevent the accurate measurement of oxygen absorption. These curves do indicate that drier catalysts considerably shorten the induction period of the oil oxidation; the results in run 28e are not out of line because the first hour's oxidation was carried out at room temperature. In the other four runs, the

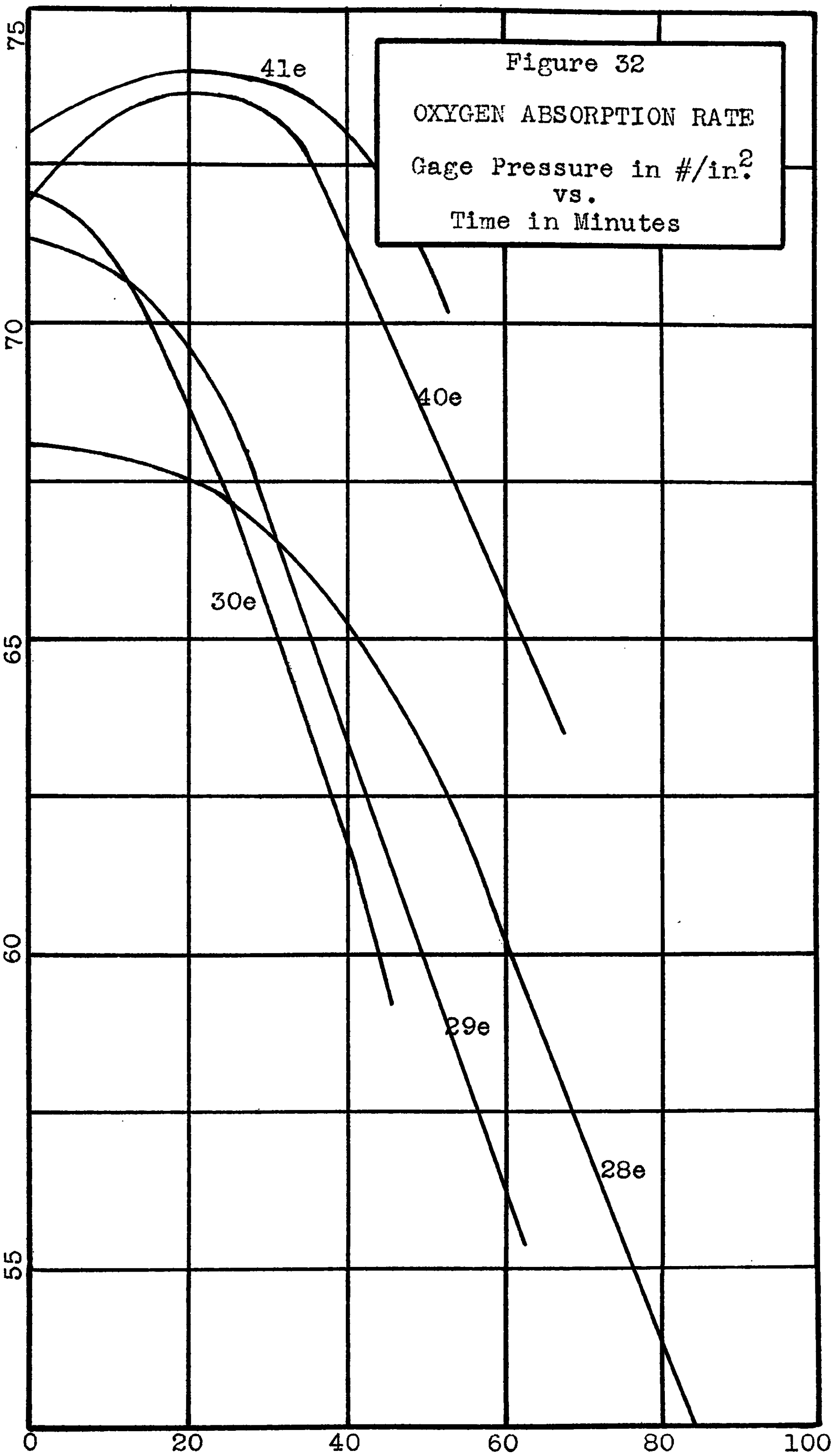


Figure 32
OXYGEN ABSORPTION RATE
Gage Pressure in #/in.²
vs.
Time in Minutes
41e
40e
30e
29e
28e
75
70
65
60
55
0
20
40
60
80
100

slopes of the curves are very similar, although the actual pressure drops are widely different.

All of these oxidized oils exhibit resin solubility at 50°C. or less. The viscosities are better than in previous runs, because of the lower operating temperatures and the shorter times of oxidation. When the temperature was abnormally high, as in run 40e, the viscosity and color were adversely affected.

When these indexed oils were heated to 200°C., they darkened considerably and to approximately the same extent.

At a pressure of 70# gage and an average temperature of 110°F., a forty point index oil can be produced in $\frac{1}{2}$ hour if 0.005% Co catalyst is added to the mixture.

<u>Series (f):</u> Previous results have shown that an oxidized oil can be produced under pressure only if some catalyst is present; agitation with an aluminum coil has no catalytic action, but cobalt soaps have a strong action.

In an attempt to determine the nature of the oxidation reaction, a series of runs were made of widely different character.

Run 35d shows the negative results obtained with no catalyst, but with an aluminum coil agitator.

Run 39c shows the negative results obtained with no catalysts or induced agitation.

Run 45f was a percolator blow of Superb linseed oil to the end of the induction period. After 8½ hours, the refractive index had increased five points and the oil was definitely past its induction period. Theoretically, at this point, the natural oil antioxidants have been removed or destroyed and peroxides have been formed, which should act as catalysts for the further oxidation of the oil.

Runs 45f and 47f used this modified oil as a starting material. The data of run 47f is reproduced in Table XXI:

TABLE XXI

100g. Superb linseed oil at the end of its induction period - no other catalyst - oxygen gas

Time	Heat	Pg	P'g	t°	Remarks
----	High	----	----	75	Heat on
----	"	----	----	--	O_2 going in
0:00	"	70.5	72	87	Autoclave rocking
0:15	"	74	74.5	97	
0:30	"	78.5	77	110	
0:53	Low	79	73.5	142	
1:00	Off	76.5	70.5	150	
1:15	"	71	63.5	168	
1:30	Off	66	59	169	Pressure released

Strongly oxidized oils were produced in both these runs. Evidently the pressure system cannot of itself carry the oil past its induction period, but does so readily if no metallic soaps are added or if percolator action is used previous to pressure oxidation. This pressure phenomenon may be due to two causes:

(a) The induction period involves equilibrium reactions in which the volume of the system tends to increase, or

(b) The induction period involves reactions which require a more thorough and intimate contact with the oxidizing gas.

In order to determine which of these two causes were effective, run 43f was tried by putting a deliberate slow leak in the system. However, the results were negative over a period of 2½ hours. Evidently the contact of oxygen and oil is not sufficiently intimate to rapidly destroy the oil antioxidants and to form peroxide catalysts.

Run 44f used 0.005% Co as a catalyst and produced an index oil in 30 minutes. This oil had resin solubility and a moderate viscosity but developed a dark color when heated to 200°C. The rate curve of this run and of run 47f are plotted in Figure 33. Obviously the metallic soap is a much stronger catalyst than the peroxides formed during the induction period in a percolator blow.

The results of this series may be summarized as follows:

(1) An active catalyst, such as cobalt Nuodex, is necessary to promote rapid and controlled oxidation of

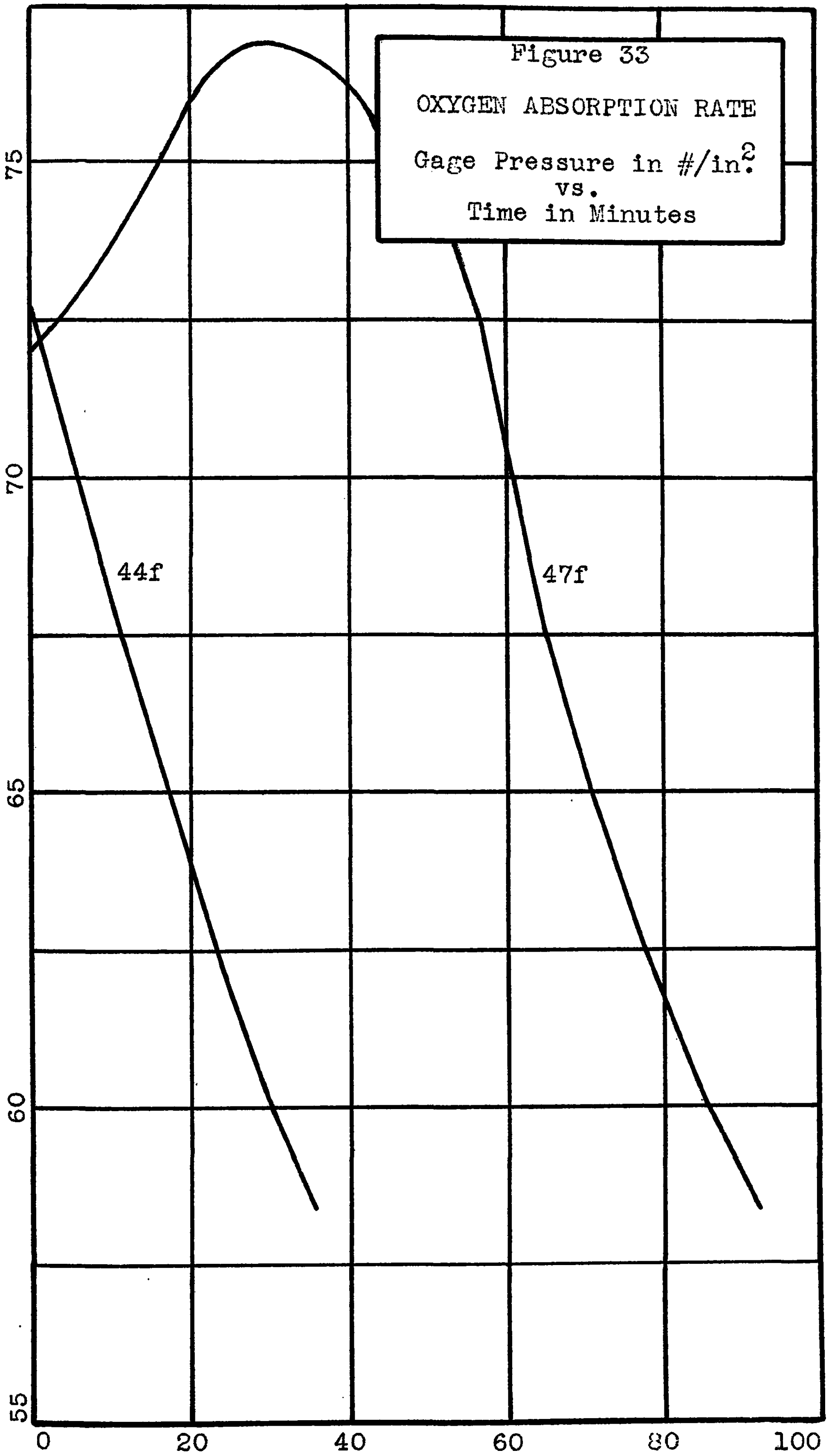


Figure 33

OXYGEN ABSORPTION RATE

Gage Pressure in #/in.^{2}
vs.
Time in Minutes

linseed oil.

(2) Induced agitation, as obtained by a spiral aluminum coil is insufficient to cause any oxidation of linseed oil in less than seven hours.

(3) More effective agitation, as obtained in percolation, causes a slow but controllable oxidation of linseed oil.

(4) Non-catalyzed pressure oxidation does not take place in a reasonable time, even though provision is made to overcome any equilibrium reaction effects.

Series (g): Since catalysts were found necessary to promote rapid, controllable oxidation of linseed oil, further investigations were made in the use of cobalt and other catalysts, and catalyst combinations.

This series of runs was made to determine the combined effect of pressures and cobalt catalyst on the time of oxidation and the properties of the final oxidized oil.

Three runs at various pressures were made to determine a practical range of pressures for oil oxidation. Previous work had indicated that the temperature should be kept below 150°F. for safe operation and also to improve the viscosity of the index oil.

The rate curves for runs 50-52g are plotted in Figure 34. Inspection of the slopes of

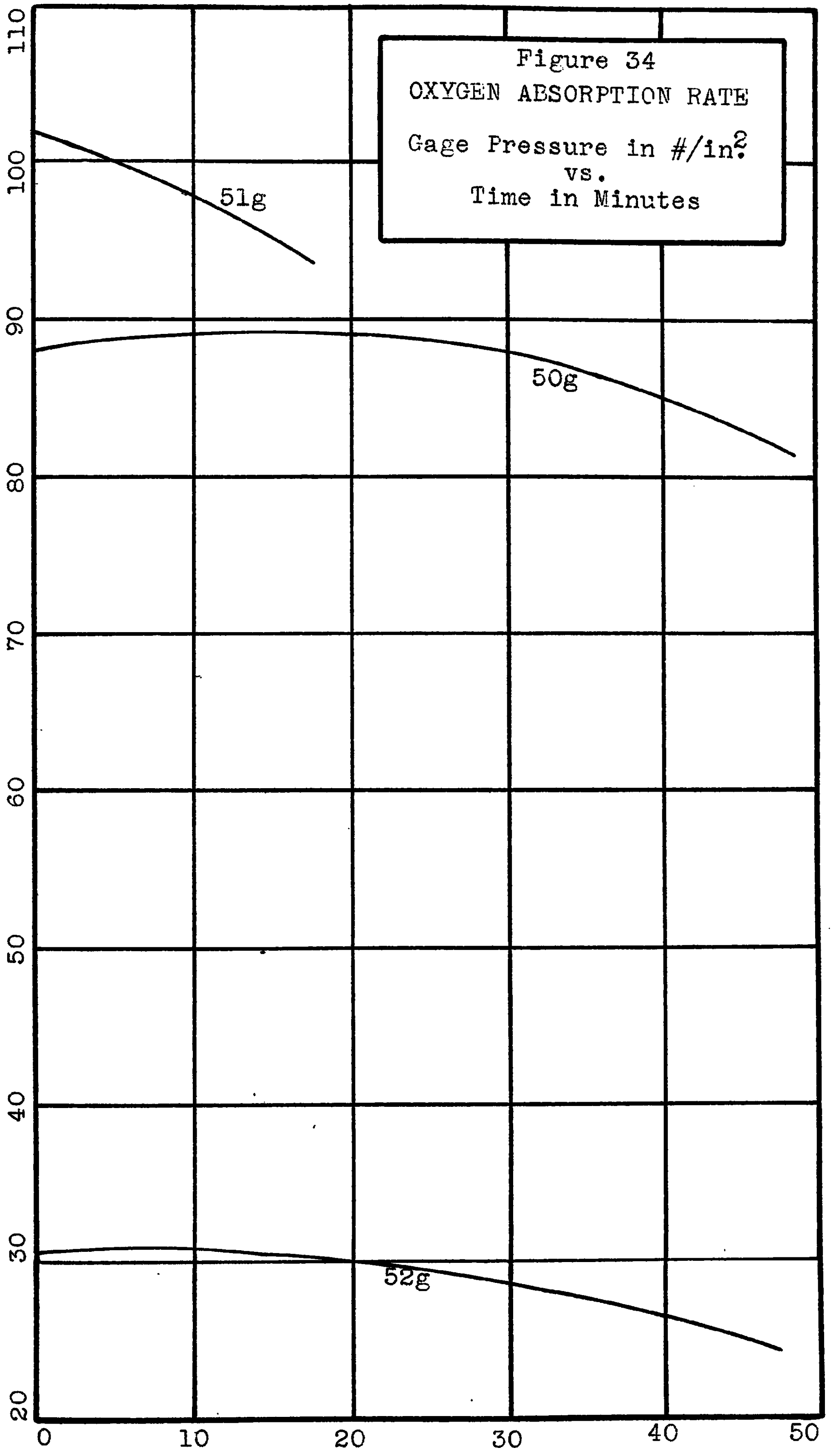


Figure 34
OXYGEN ABSORPTION RATE
Gage Pressure in #/in.²
vs.
Time in Minutes
51g
50g
52g
110
100
90
80
70
60
50
40
30
20
0
10
20
30
40
50

these curves shows that higher pressures cause an extremely rapid oxidation of the oil. Although pressures above 100# gage become dangerously unsafe, a combination of high pressure, catalyst and moderate temperatures can be found, which will enable continuous production of index oil.

Color and viscosity depend more on the extent of oxidation than on the pressure of the system.

Series (h): One run was made to determine the minimum amount of catalyst for practical purposes. The catalyst quantity is of importance from a sales standpoint; many oil buyers object to any artificial materials in the oil.

Run 61h used 0.001% Co, an insignificant quantity from the varnish-makers viewpoint. At 87# gage and 113°F., a 32 point index oil was produced in less than 3/4 of an hour. This oil has resin solubility and satisfactory color and viscosity. However, the production requires twice the time of run 50g. The rate curves of these two runs are plotted for comparison in Figure 35.

Series (i): A series of runs was made in which various single and multiple catalysts were evaluated.

Single metallic soap catalysts, other than cobalt Nuodex, do not exhibit strong effects, as shown by runs 53, 55 and 56i. Lead Nuodex is somewhat

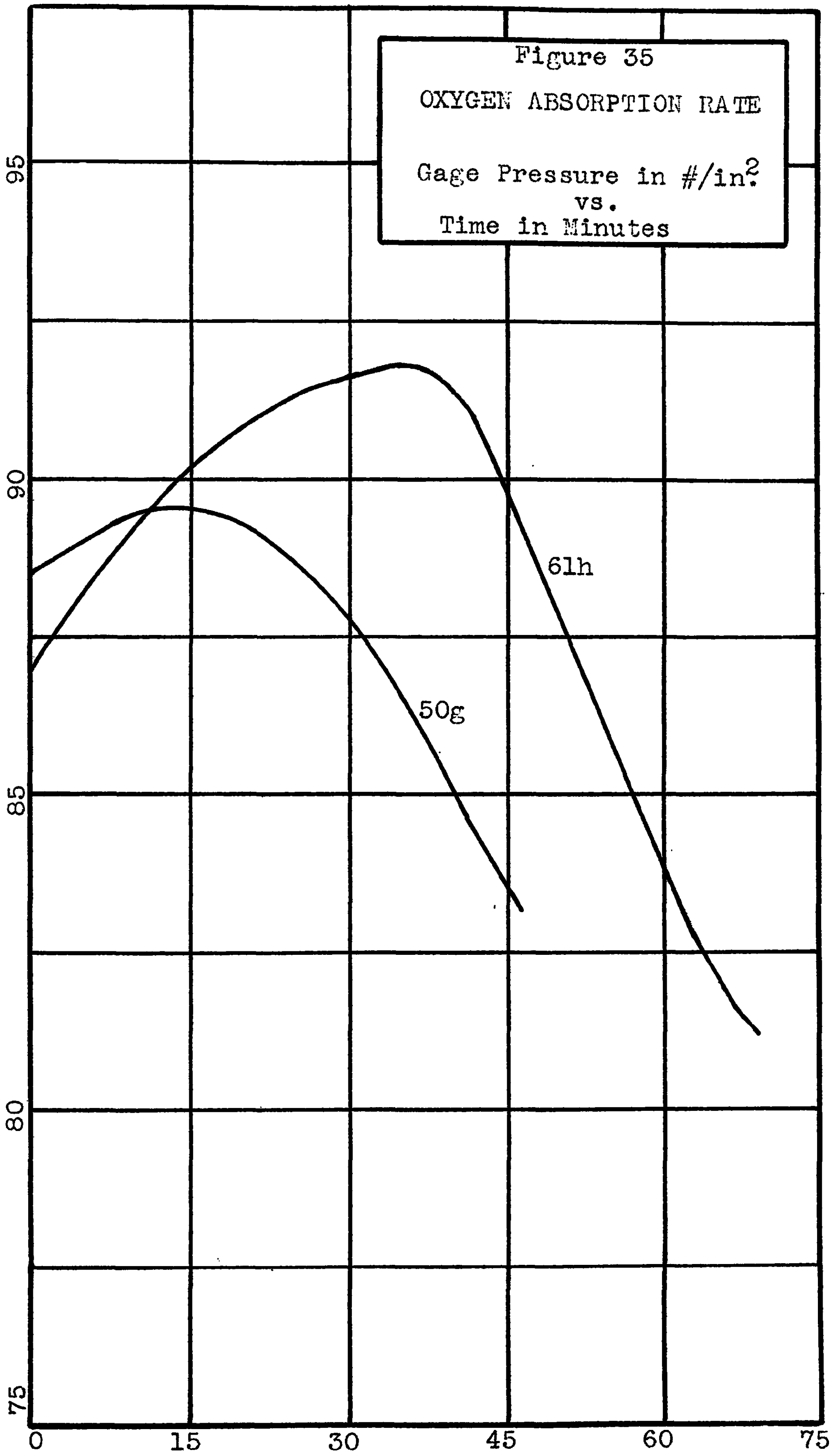


Figure 35
OXYGEN ABSORPTION RATE
Gage Pressure in #/in^2
vs.
Time in Minutes
95
90
85
80
75
0
15
30
45
60
75
61h
50g

more active than manganese; both are much superior to iron Nuodex and far inferior to cobalt Nuodex. In 35 minutes, 0.1% lead Nuodex produces a 16 point oil which shows resin solubility and has excellent viscosity and color. However, the lead drier tends to precipitate as a white, crystalline deposit; more detail will be given on this problem in the later discussion.

Interesting results were obtained with acids and bases. Since these materials are known to catalyze the isomerization of double bonds in unsaturated acids, examples of both classes were tried as single catalysts for the pressure oxidation of oils.

Run 49i was made with 0.05% glacial acetic acid as a catalyst. Although 4 hours oxidation at 75# gage and 141°F. are required to produce a 34 point index oil, support is given to the isomerization theory of oil conjugation and oxidation, because a much longer time without any catalyst does not produce an index oil. Furthermore this oil has resin solubility abnormally low viscosity and moderate color.

Run 79i was made with 0.05% KOH in 0.2% water as a catalyst. The results were entirely similar to run 49i and lend further support to the isomerization postulate.

Benzoyl peroxide is a well-known

polymerization catalyst. Two runs, 76i and 77i were made using 0.1% of this substance, dispersed in the oil in run 76i and dissolved in acetone in run 77i. At 85# gage and 126°F., two hour treatments of the oil did not cause any oxidation or change in viscosity or color. Higher temperatures are evidently necessary to activate the catalytic powers of this compound.

In run 78i, 0.2% acetic acid and 0.1% benzoyl peroxide were combined as catalysts but 3½ hour treatment at 85# gage and 130°F. did not produce any change in the oil properties.

Since cobalt Nuodex is the only effective catalytic material, it was used as a basis for testing catalyst combinations which might have a more effective action than the single cobalt catalyst.

In run 48i, 0.005% Cobalt Nuodex and aluminum coil agitation were combined. The combination worked better than the single cobalt catalyst.

In run 54i, 0.0025% manganese Nuodex was added to the 0.005% cobalt catalyst. Marked acceleration of the oxidation reaction was produced; the effect was slightly stronger than that in run 48i.

To this multiple catalyst was added 0.05% acetic acid. The effect was even stronger than before, as shown by the data on run 74i.

In run 80i, 0.1% benzoyl peroxide

was substituted for the acetic acid. However the rate of oxidation was not better than that in run 54i, in which the peroxide is omitted.

In run 81i, all four catalysts were combined, namely 0.005% cobalt Nuodex, 0.0025% manganese Nuodex, 0.05% acetic acid and 0.1% benzoyl peroxide. No noticeable improvement could be found over run 74i, in which the benzoyl peroxide is omitted.

Further studies on drier combinations could have been made, but they were thought unnecessary because of the present excellent results. A combination of 0.005% cobalt Nuodex and 0.0025% manganese Nuodex is both an effective catalyst and a desirable catalyst. The addition of lead Nuodex improves the oil color but causes haze in the oil solution. Smaller concentrations of driers are still effective, but these were discarded for testing work in favor of a more reactive combination.

The rate curves of runs 50g, 49i, and 79i are plotted in Figure 36. The slower catalytic action of acid and base catalysts is readily apparent.

The rate curves of runs 50g, 48i, 54i and 74i are plotted for comparison in Figure 37. No great differences exist between these rates of oxidation, but a consideration of the index of the final product in each case will show the beneficial action of acetic acid and manganese Nuodex when added to cobalt Nuodex.

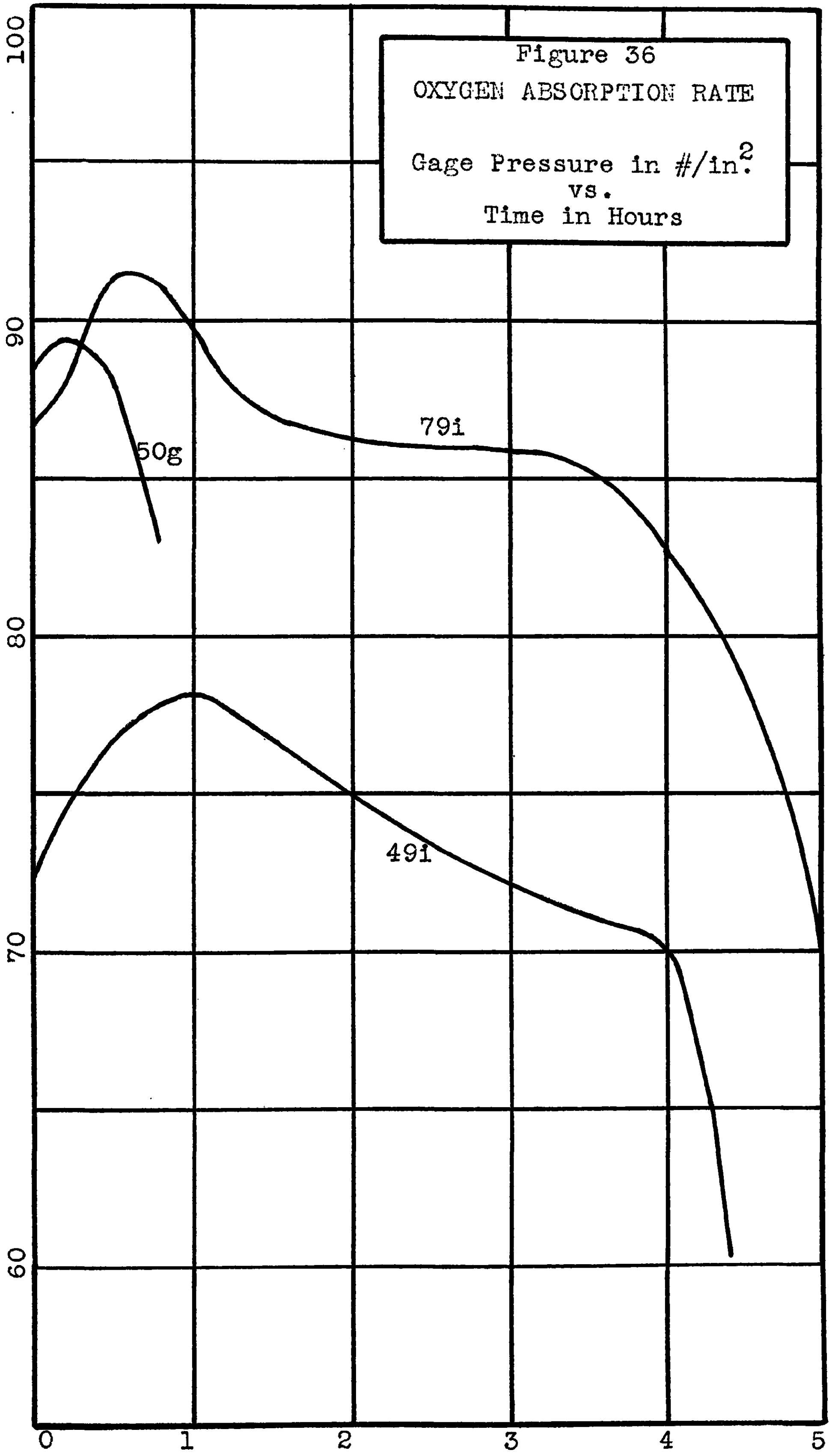


Figure 36
OXYGEN ABSORPTION RATE
Gage Pressure in #/in.^{2}
vs.
Time in Hours
100
90
80
70
60
0
1
2
3
4
5
50g
79i
49i

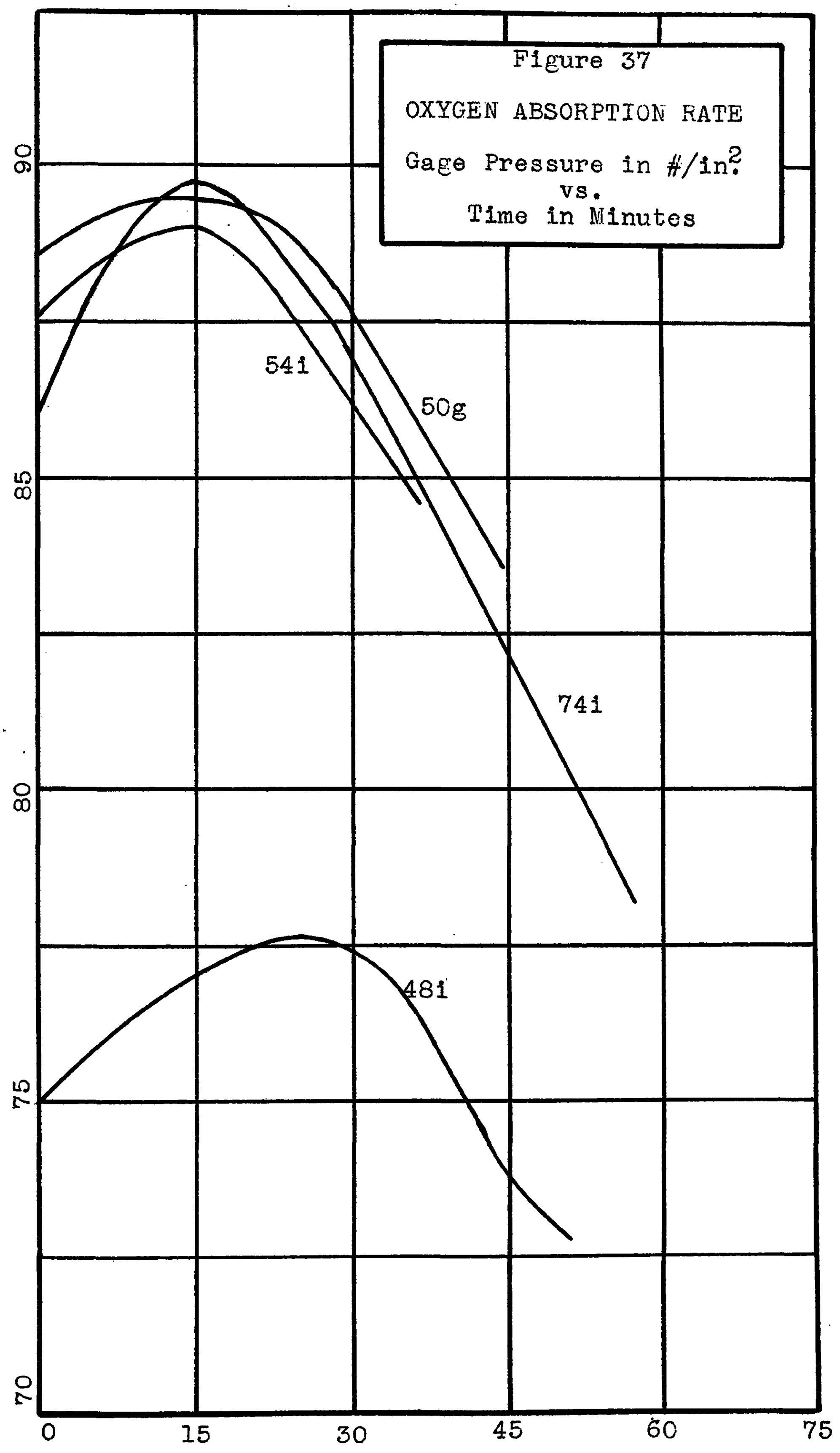


Figure 37
OXYGEN ABSORPTION RATE
Gage Pressure in #/in^2
vs.
Time in Minutes
54i
50g
74i
48i
90
85
80
75
70
0
15
30
45
60
75

Series (k): The oxidation of small (100g.) samples of linseed oil with pure oxygen was successfully controlled and investigated. The work in this series relates to the development of this process to practical quantity production. A sample of 1200g. was used as a standard, since this quantity filled more than half the autoclave volume. Standard practice dictates that pressure autoclaves should never be filled more than two-thirds of their volume.

The results of runs 57-59k showed that higher oxygen pressures were needed to produce a 40 point index oil. The final run of this group, run 59k, was conducted at 189# gage and 149°F.; it produced a 34 point oil in 1-2/3 hours but the oxygen absorption was comparatively slow after the pressure dropped below 50# gage. In all three of these runs the final oil index was solely dependent upon the initial pressure; the reaction practically stopped when the oxygen pressure dropped much below 50# gage. The data of run 58k is shown in Table XXII as being typical of this group.

The rate curves for these three runs are plotted in Figure 38 in order to show the effect of low pressure on the final stages of oxidation. Probably the oil has about reached its final index long before it was withdrawn as a sample.

TABLE XXII

1200g. Superb linseed oil - 0.005%Co & 0.0025%Mn oxygen gas

Time	Heat	Pg	P'g	t°	Remarks
----	High	----	----	76	Heat on
----	"	----	----	--	O_2 going in
0:00	"	113	115	88	Autoclave rocking
0:15	"	83.5	82.5	108	
0:30	Off	54.5	51.5	134	
0:45	"	34.5	31.5	150	
1:00	"	21.5	19.5	158	
1:15	"	14	12.5	156	
1:30	Off	10	9	152	Pressure released

All these oils showed resin solubility although they varied in index from 16 to 34 points.

In order to decrease the time necessary to produce a higher index oil and still to stay away from excessively high pressures, two runs were made on the effect of increasing the pressure as soon as it fell below 70# gage.

To illustrate this method the data of run 60k is reproduced in the following table.

TABLE XXIII

1200g. Superb linseed oil - 0.005%Co and 0.0025%Mn oxygen gas

Time	Heat	Pg	P'g	t°	Remarks
----	----	----	----	72	O_2 going in
----	High	191.5	201.5	72	Heat on
0:00	"	195	201.5	82	Autoclave rocking
0:05	"	198	201.5	90	
0.10	"	201	204	92	
0:15	"	203.5	205	95	
0:30	Low	191	184	122	
0:45	Off	121	109	162	
1:00	"	71.5	63	178	O_2 going in
1:00	----	79	69.5	---	
1:15	Off	51	45	178	O_2 going in
1:15	----	105	92.5	---	
1:30	Off	71	62	178	Pressure released

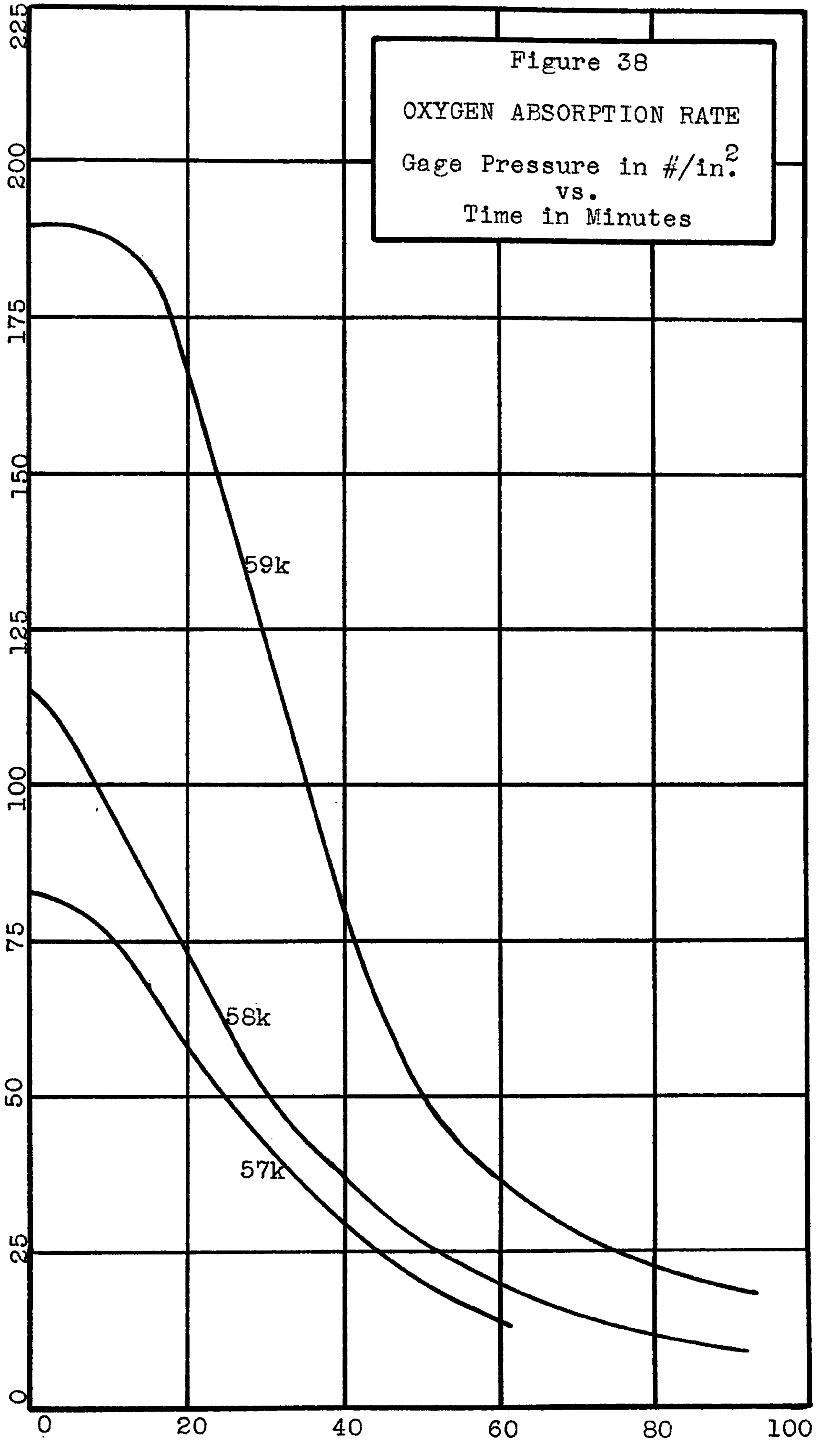


Figure 38

OXYGEN ABSORPTION RATE

Gage Pressure in #/in.^{2}
vs.
Time in Minutes

By increasing the pressure near the end of the run, a 40 point index oil was produced in 1-1/6 hours.

In run 62k the catalyst was modified by reducing the cobalt content and by adding lead Nuodex and an increased amount of manganese Nuodex. The pressure was increased near the end of the run as in 60k but the time of oxidation was much slower than the preceding run.

The rate curves of runs 60 and 62k are plotted in Figure 39 for comparison of the drier effectiveness.

Series (m): In this series the production of index oils was studied when air instead of pure oxygen was used. Runs 63 and 66m were made on 100g. samples of Superb linseed oil.

Run 63m is meaningless because the 0.001%Co catalyst was accidentally added to the autoclave surface instead of the oil sample.

In run 66m, a 45 point index oil was produced in 1-3/4 hours at a pressure of 368# gage and a temperature of 139°F. The air pressure was built up by successively adding pure oxygen and pure nitrogen in the proper proportions. The rate curve for this run is plotted in Figure 40.

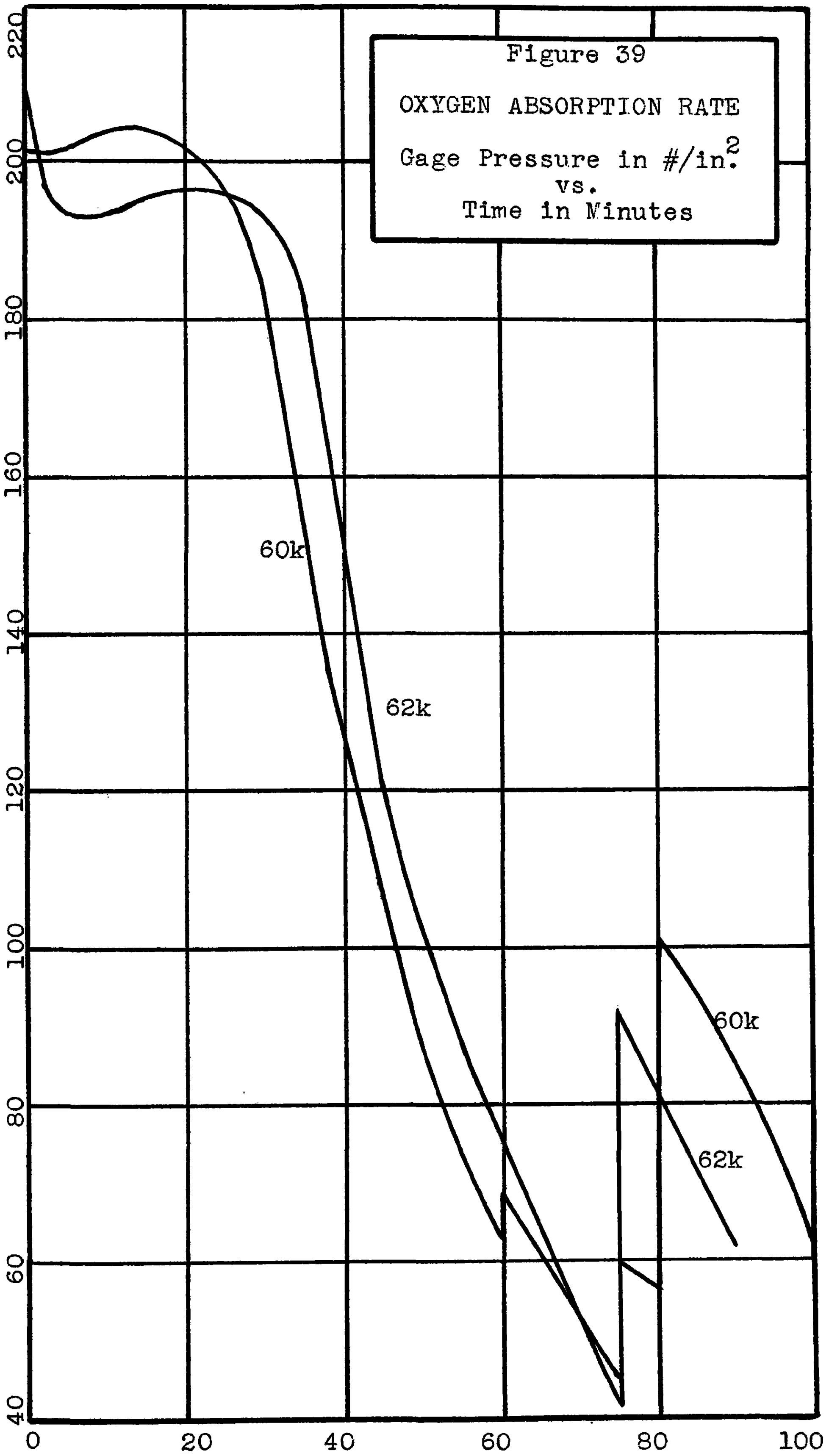


Figure 39

OXYGEN ABSORPTION RATE

Gage Pressure in $\#/in.^2$
vs.
Time in Minutes

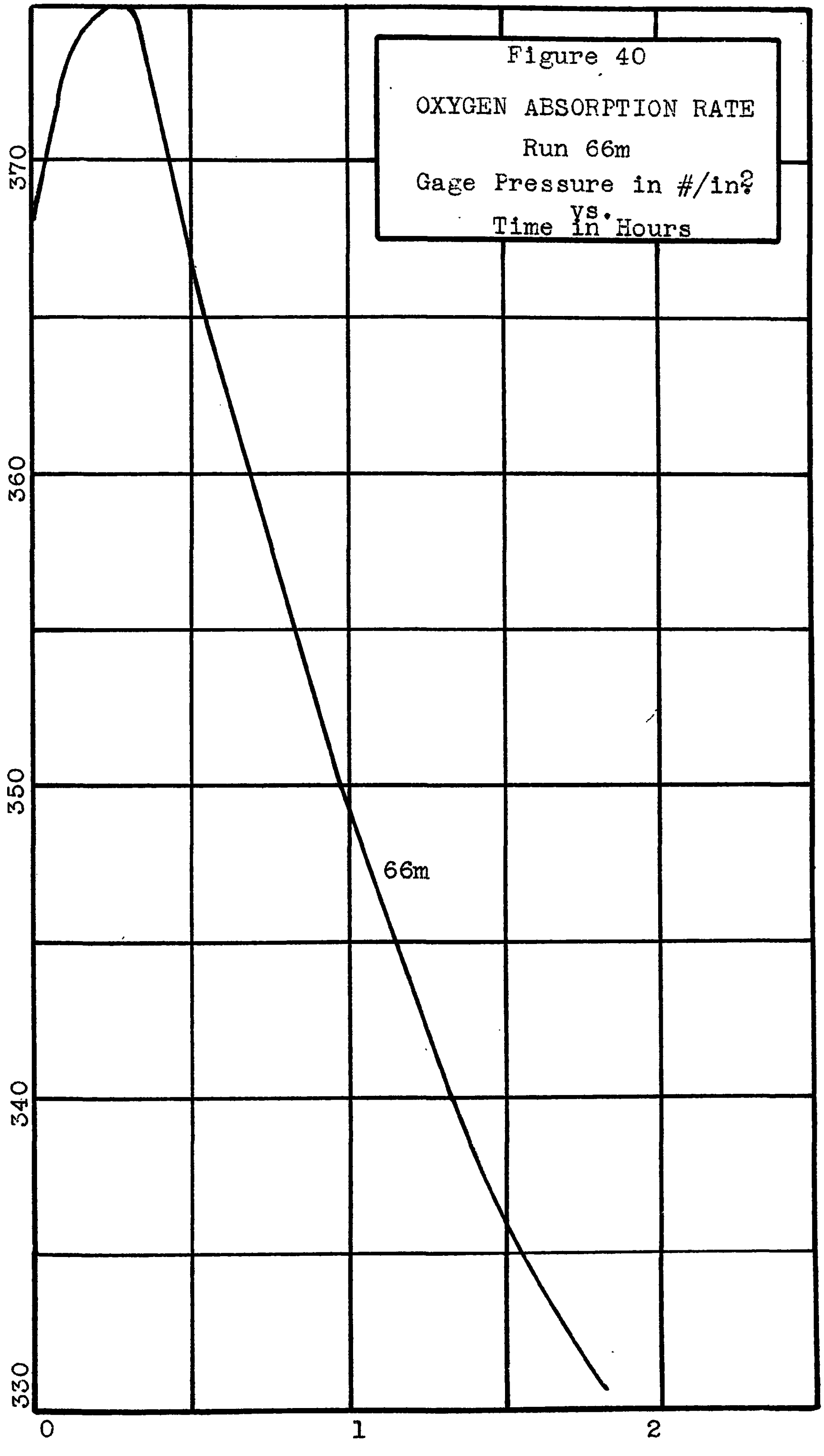


Figure 40

OXYGEN ABSORPTION RATE

Run 66m

Gage Pressure in #/in^2 vs. Time in Hours

Series (p): When air pressure was attempted with a 1200g. sample of oil, the same difficulties arose as in previous work with large samples.

Run 67p had too low an initial pressure to produce much oxidation.

Runs 68 and 69p yielded 33 and 43 point index oils in 2 hours and 1½ hours respectively. Both oils showed resin solubility, had moderate viscosities, and darkened when heated to 200°C.

The data of run 69p is reproduced in the following table.

TABLE XXIV

12--g. Superb linseed oil - 0.005%Co and 0.0025%Mn - air pressure

Time	Heat	Pg	P'g	t°	Remarks
----	High	----	----	75	Heat On
----	"	----	----	--	O_2 going in
----	"	300	----	--	N_2 going in
0:00	"	1495	1485	103	Autoclave rocking
0:05	Medium	1485	1465	108	
0:10	Off	1505	1455	119	
0:15	"	1510	1420	136	
0:20	"	1505	1395	145	
0:30	"	1490	1355	155	
0:45	"	1450	1320	155	
1:00	"	1415	1295	153	
1:15	Off	1400	1290	147	Pressure released

The rate curves for this series are plotted in Figure 41.

Series (r): The application of this method to oils other than Superb linseed oil was investigated by pres-

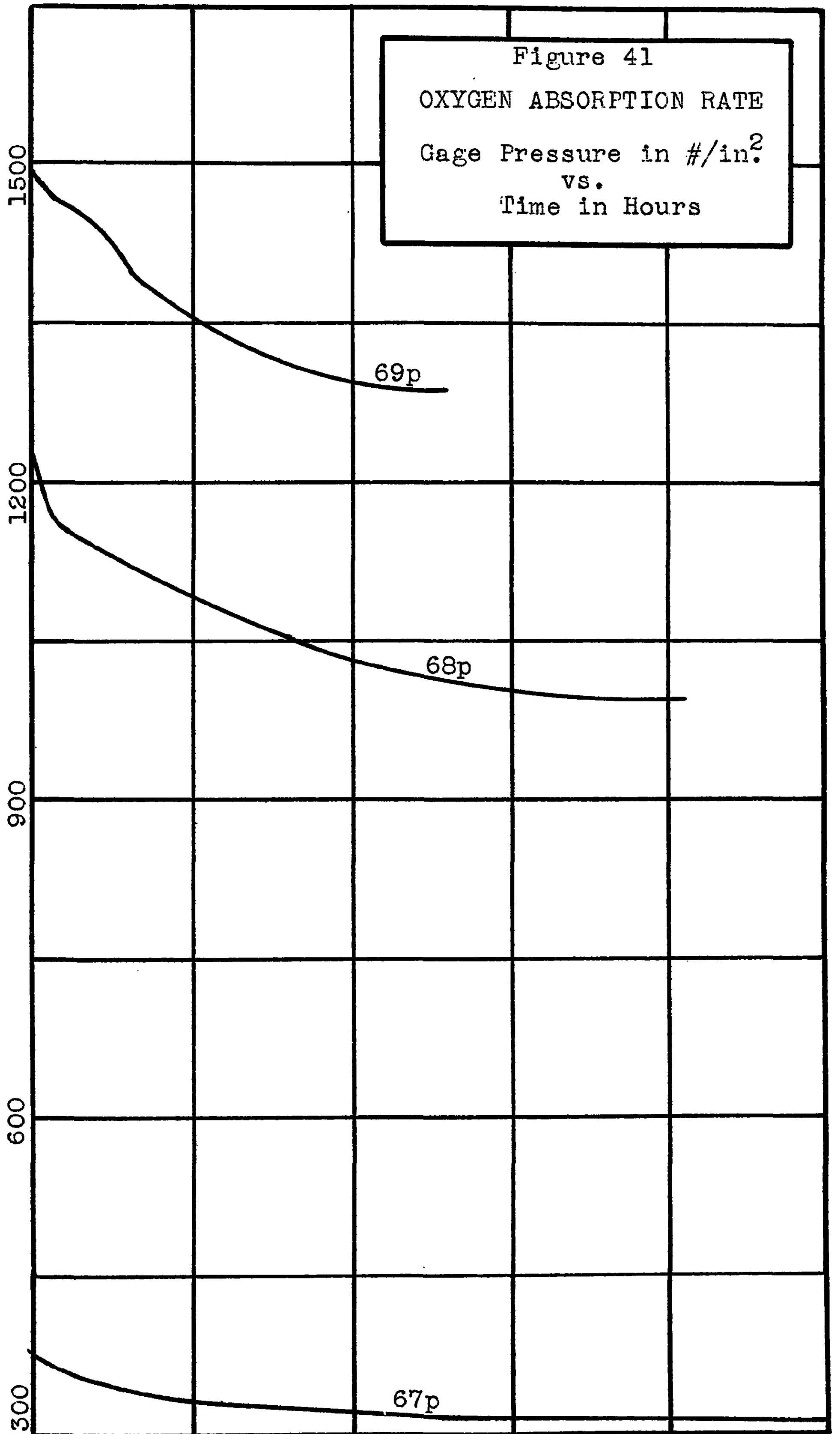


Figure 41
OXYGEN ABSORPTION RATE
Gage Pressure in #/in.^{2}
vs.
Time in Hours
1500
1200
900
600
300
0
½
1
1½
2
2½
69p
68p
67p

sure oxidation of 100g. samples using pure oxygen gas. The logical assumption follows that, by suitable modifications, these oils can be oxidized in larger quantities with air as the compressing gas.

All of the investigated oils were readily oxidized to index oils having resin solubility and other characteristic properties.

The rate curves for this series are plotted in Figure 42.

Superb soybean oil oxidizes slightly less rapidly than Superb linseed oil. However, the final index oil is less viscous and considerably lighter than Superb linseed index oil. Moreover it does not darken as strongly when heated to 200°C.

Non-break perilla oil oxidizes at about the same rate as soybean oil, but its viscosity and coloration are both very bad.

Refined menhaden oil oxidizes almost as rapidly as Superb linseed oil but its very dark, reddish color limits its use to brake lining saturants and dark varnishes.

Non-break raw linseed oil oxidizes at almost the same rate as Superb linseed oil and has all the desirable characteristics of the latter.

SH'd linseed oil oxidizes much slower than the other linseed oils, even slightly slower

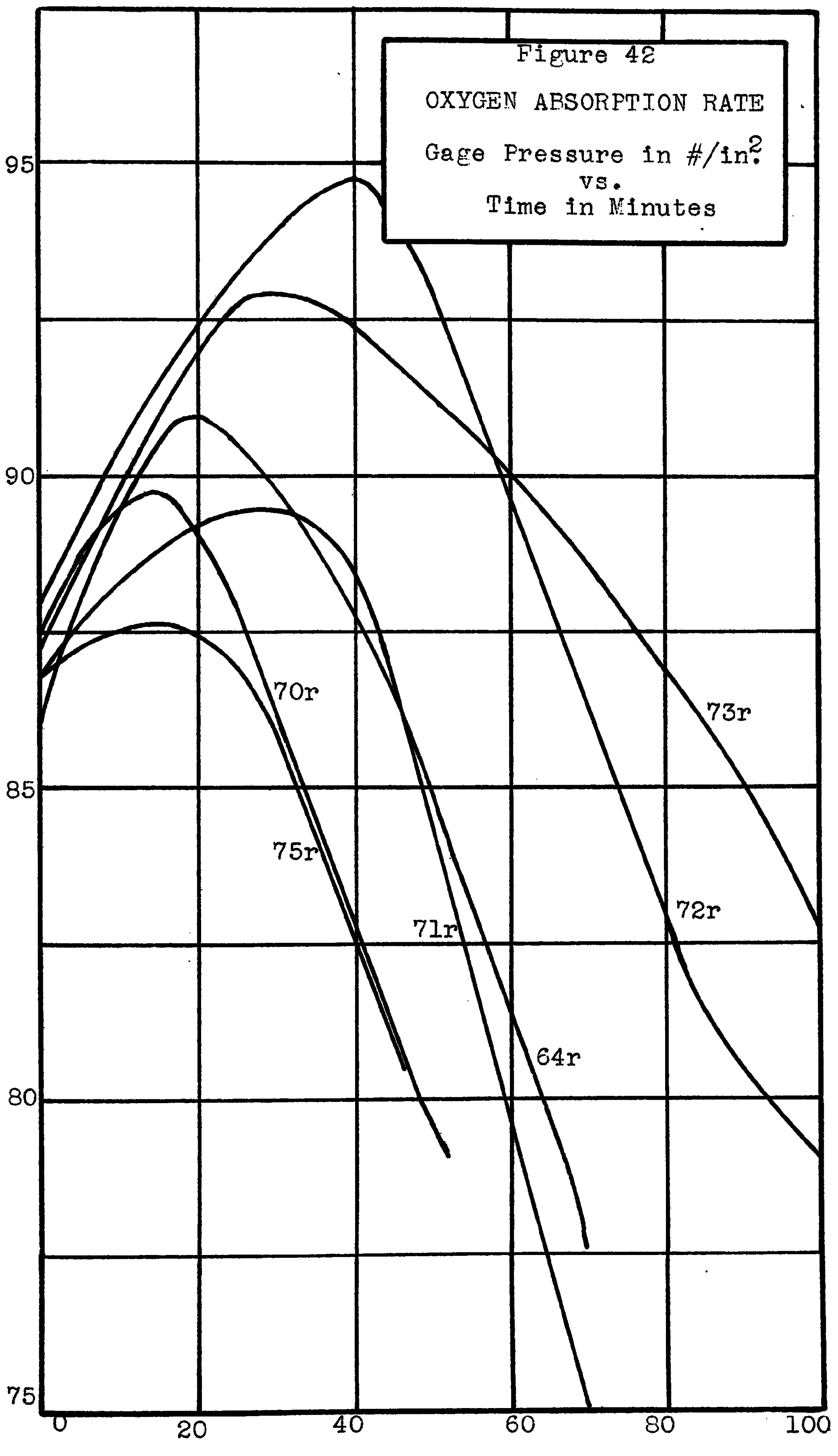


Figure 42

OXYGEN ABSORPTION RATE

Gage Pressure in #/in.^{2}
vs.
Time in Minutes

than soybean oil. Moreover its color is slightly worse than that of other linseed oils.

One run, #73r, was made on the 1:1 mixture of linoleic and oleic acids. These acids absorbed oxygen at a relatively slow rate and their index change was only 17 points. However, the oxidized acids readily dissolved resin #451, a fact which leads to the suggestion that it may be the oxidized acids, aldehydes, etc., produced during percolation or pressure oxidation, that are the actual resin solvents. This phase will be discussed in detail in a later section.

Series (t): These runs were made with pure nitrogen gas on Superb linseed oil in the presence of catalysts to determine if oils could be usefully modified by a non-oxynic atmosphere.

Run 82t at 1060# gage and 155°F. with 0.05% acetic acid catalyst gave negative results.

Run 83t at 953# gage and 155°F. with 0.05% acetic acid and 0.1% benzoyl peroxide catalysts produced a 13 point oil in $7\frac{1}{2}$ hours. This oil had excellent color and viscosity, but dissolved resin 451 with difficulty.

Polymerization catalysis is strongly affected by light, a fact which may account for the relative impotency of benzoyl peroxide. The oxidation reaction may well be catalyzed by substances such as linolyl peroxide, olyl peroxide, perstearic acid and the like.

Further work, which might lead to improvement and to new methods, might include the following:

(1) Thin film oxidation on baffles
(2) A counter-current oil - air system under pressure.
(3) Preliminary air saturation of the oil before applying pressure.
(4) The use of color stabilizers and decolorizers during the oxidation process.
(5) The use of a dehydrogenation catalyst on a non-drying oil in a pressure-oxygen system.
(6) The use of solid adsorbents.
(7) Induced aggregation to micellae by means of electric impulses or coagulating agents in a pressure-oxygen system.

STUDY OF PROPERTIES OF OXIDIZED OILS

(1) Drying Time - A number of tests were made on pressure oxidized oils to compare qualitatively their drying periods in relation to each other and to untreated oils. These results are summarized in Table XXV. The index of the oil is tabulated as a qualitative check on its state of oxidation.

The drying time evaluation depends upon the extent of oxidation, the quantity of catalyst, and the viscosity of the oxidized oil. The latter factor influences the film thickness; high viscosity oils yield an apparently longer drying time than do oils of lower viscosity.

In Series a, a trace of catalyst is no doubt present. All these oils dry in approximately the same time, although their indices vary from 29 to 45. The higher viscosities of the more highly oxidized oils partially neutralize the oxidation effects.

Samples 36c and 35d have the drying characteristics of untreated linseed oil; they contain no catalysts and have no increase in refractive index.

Series e shows that oxidized oils containing 0.005% cobalt catalyst dry in one-third the time of untreated linseed oil.

Sample 47f, which contained no artificial catalysts, was highly oxidized, but only dried in 5½ days,

TABLE XXV.

Run Number	Type Oil	Δn	G	Drying Time in Days	Film Condition After^x:			Relative Drying Times
					1 day	2 days	5 days	
100	Superb linseed	0	A	9	W	W	W	15
101	Tung	0	S	$3\frac{1}{2}$	W	DDW	D	7
20a	Superb linseed	44	L	6^{z}	W	WD	DW	13
21a	"	29	F	6^{z}	W	WD	DW	13
23a	"	40	I	6^{z}	W	WD	DW	13
24a	"	45	P-Q	$5\frac{1}{2}^{z}$	W	WD	DDW	12
25a	"	39	H	6^{z}	W	WWD	DW	13
22b	"	35	L-M	6^{z}	W	WD	DW	13
36c	"	1	A	--	W	W	W	15
31d	"	11	B	6^{z}	W	WD	WD	14
35d	"	0	A-B	--	W	W	W	15
28e	"	50	L	$3\frac{1}{2}^{d}$	W	DW	D	8
29e	"	40	F-G	$3\frac{1}{2}^{d}$	W	DW	D	8
30e	"	35	D	$3\frac{1}{2}^{d}$	W	DW	D	8
40e	"	53	N	$3\frac{1}{2}^{d}$	W	DDW	D	6
41e	"	40	F	$3\frac{1}{2}^{d}$	W	DDDW	D	3
44f	"	37	F-G	$3\frac{1}{2}^{d}$	W	DW	D	8
47f	"	55	S	$5\frac{1}{2}$	W	WD	DDDW	10
50g	"	38	G	4^{d}	W	DDDW	D	6
61h	"	32	F	4^{d}	W	DDW	D	8
48i	"	34	F	$3\frac{1}{2}^{d}$	W	D-	D	1
49i	"	34	D	6^{o}	W	WD	DDDW	12
54i	"	29	D	$3\frac{1}{2}^{d}$	W	DDDW	D	4
79i	"	42	J-K	6^{o}	W	WD	D-	10
74i	"	49	M	4^{d}	W	DDW	D	8

Run Number	Type Oil	Δn	G	Drying Time in Days	Film Condition After:[x]			Relative Drying Times
					1 day	2 days	5 days	
80i	Superb linseed	37	F	$3\frac{1}{2}^{d}$	W	DDDW	D	5
81i	"	32	E	$3\frac{1}{2}^{d}$	W	DDDW	D	5
60k	"	40	I	4^{d}	W	DDDW	D	6
62k	"	31	H	4^{d}	W	DW	D	9
66m	"	45	I	$3\frac{1}{2}^{d}$	W	DDDW	D	3
69p	"	43	H	$3\frac{1}{2}^{d}$	W	DDDW	D	5
70v	Raw linseed	36	G	4^{d}	W	DW	D	9
71v	Perilla	44	T	$3\frac{1}{2}^{d}$	W	D-	D	2
72v	SH'd linseed	42	I	4^{d}	W	DDW	D	8
73v	Linoleic-oleic	17	S	$--^{d}$	W	W	W	15
75v	Menhaden	44	I	6^{d}	W	DW	DDW	11
83t	Superb linseed	13	B	7	W	W	D-	13

o These oils did not form perfectly dry films.

x Code: D = dry, W = wet; the predominant state is indicated first, and is emphasized by repitition; D- indicates dry but tacky film.

d A drier catalyst is present in the oil during blowing and drying periods.

z A trace of drier is probably present.

compared to 9 days for the same oil before pressure oxidation.

Sample 61h dried almost as rapidly as those of Series e, although the drier content in the former case was only 0.001% cobalt.

Samples 49i and 79i were oxidized in the presence of acid and base catalysts respectively. These oils never dried completely, but they set to a soft, somewhat tacky film in less than 5 days.

Runs 54i, 74i, 80i and 81i show that the presence of small percentages of catalysts other than cobalt has very little effect on the drying rate of partially oxidized oils.

The drying times of oxidized oils other than Superb linseed, follow the general trend of the unsaturation degree of the untreated oil. Perilla index oil has a rate comparable to Superb linseed index oil; raw linseed and SH'd linseed index oils dry at almost the same rate as the preceding two; menhaden index oil, which has less residual unsaturation, dries more slowly than any of the other oils. These results are illustrated in Series v.

Sample 73v, which was an oxidized mixture of linoleic and oleic acids, did not dry because of its inherent linear molecular structure.

Sample 83t is interesting because it was modified by pressure polymerization mechanisms. It has an index rise of 13 points, and dries in slightly less time than untreated linseed oil. Probably it is analogous to a bodied linseed oil, although its viscosity is quite low.

The isomerism of double bonds, to be discussed later, may well lead to a conjugated system which dries more rapidly than the normal double bond system of linseed oil.

To summarize, we can say that partially oxidized oils (index oils), containing no artificial catalysts, do not have any startling drying characteristics. However, when an index oil is heat bodied, the lithographic varnishes produced have drying times which are much less than that of a standard lithographic varnish produced from straight linseed oil. Two varnishes, having the following properties, were prepared:

Varnish Prepared From	Pipette Viscosity	Acid Number	Bolton-Williams Iodine Number
40 point Index Oil	227 secs.	10.08	135
Superb linseed oil	235 secs.	15.00	114

These varnishes were ground with a medium chrome yellow; cobalt drier was added up to one ounce per pound of ink. Prints were made on paper and pad outs were made on a marble slab. The following drying characteristics were found:

On Paper

Ink with Index Oil.........................dry in 30 minutes

Ink with Superb Linseed Oil..............dry in 45 minutes

On Marble

Ink with Index Oil.........................dry in 25 minutes

Ink with Superb Linseed Oil..............dry in 40 minutes

Some drying tests of index oil were made by flowing mixtures of various solvents and the oil, and in some cases a drier, on sheet iron strips. During the tests, the average temperature was 26° C., and the average humidity was 70%. The solvent was found to have a slight influence in the drying time. Driers had a very pronounced effect. The samples to which driers had been added, dried in five hours in the case of manganese and cobalt driers, in twenty hours in the case of iron drier, and in twenty-four hours in the case of the lead drier. All other samples required more than twenty-four hours to dry; untreated linseed oil required the most time.

(2) Resin Solubility - Probably one of the most important characteristics of index oils is their ability to dissolve many synthetic resins, which are insoluble in untreated oils other than chinawood oil.

The 451 resin test is indicative of this unique property of index oils. If ten grams of 451 resin is heated slowly with ten grams of linseed, soybean or perilla oil, it forms a clear solution after a few minutes at 110° C. As the temperature is raised to 140° C., drops of the solution show a cloudiness on cooling. At higher temperatures, the resin begins to coagulate and precipitate from the solution. This phenomenon is typical of any heat convertible non-soluble resin.

When this same resin is heated with raw tung oil, a clear solution is formed at about 110° C. At 140° C., this solution begins to darken and become more viscous. This viscous condition increases with the temperature, until at temperatures above 200° C. the mass suddenly sets to a clear, dark red gel. This gel is permanently hardened by heat.

Index oils of linseed, perilla, soybean or menhaden, readily dissolve resin 451. The temperature of solubility varies somewhat with the oil and the extent of its oxidation. An oil of 35-45 point index forms a clear solution with the resin at 60° C. or less. As the solution is heated, the mass foams and produces heat. At temperatures above 200° C. the solution sets to a clear, red gel; cooling the solution effected at a lower temperature than 200° C. will likewise produce a clear, red gel.

In an attempt to elucidate the mechanism of this solubility, both the oil and the resin were heated alone. The oil undergoes a reaction around 110° C.; this reaction is highly exothermic, and causes pronounced foaming in the oil. At temperatures around 170° C., color begins to develop, and the viscosity of the oil increases. When the resin is heated alone, a reaction of some sort begins around 115° C. The resin foams slightly up to 160° C., after which there is a very pronounced foaming action. After heating to 200° C., the resin is very rubbery, and can be stretched to unusual lengths.

Further mention of the solubility mechanism will be made in connection with the later theoretical discussion.

In a number of tests with various resins, index oils were in every case as good a solvent or better than tung oil. All synthetic resins were much more soluble in index oils than in linseed oil. Run congo gum dissolved in indexed Superb linseed oil in three or four minutes at a temperature that required ten minutes to dissolve it in tung oil.

The solubilities of some commercial resins in 40 point Superb linseed index oil were determined by slowly heating 50 per cent mixtures of resin and oil up to 200° C. The index oil was produced by percolator blowing at 55° C. for 36 hours; the oil had a viscosity of D on the Gardner-Holt scale. The results of these tests are summarized in the following table:

TABLE XXVI.

Resin	Solubility	Remarks
Bakelite BV-2427	Insoluble	
Bakelite XJ-6447	Soluble (30° C.)	Gelled at 195° C.($\frac{1}{2}$')
Bakelite XJ-7331	Soluble (30° C.)	Gelled at 175° C.(2')
Bakelite XJ-6871	Soluble (30° C.)	Gelled at 195° C.(5')
Bakelite XR-6741	Insoluble	
Bakelite XR-6903	Soluble (50° C.)	No gel at 250° C.
Bakelite XR-3328	Insoluble	
Bakelite XR-7026	Insoluble	
Bakelite XR-8821	Insoluble	
Bakelite XR-2175	Soluble (70° C.)	Gelled at 215° C.(2')
Bakelite XR-2987	Soluble (120°C.)	Gelled at 190° C.(2')
Bakelite XR-8789	Insoluble	
Bakelite XR-821	Soluble (125°C.)	
Bakelite XR-2963	Soluble (155°C.)	
Bakelite XR-4036	Soluble (140°C.)	
Bakelite XR-1329	Soluble (170°C.)	
Bakelite XR-254	Soluble (140°C.)	
Bakelite XR-1330	Soluble (150°C.)	Soluble in tung oil at 180° C.
Bakelite XR-6344	Soluble (80° C.)	
Bakelite XR-820	Soluble (120°C.)	
Bakelite BR-6912	Insoluble	
Bakelite BR-7095	Insoluble	
Bakelite BR-1922	Insoluble	
Bakelite BR-6083	Insoluble	
Bakelite BR-0230	Insoluble	
Bakelite BR-6462	Insoluble	
Bakelite BR-7668	Insoluble	
Bakelite BR-4538	Insoluble	(Insoluble in tung oil, but soluble in acetone)
Bakelite BR-302	Soluble (70° C.)	
Bakelite BM-261	Insoluble	
Bakelite BM-1823	Insoluble	
Bakelite XK-3214	Insoluble	
Rezyl #113	Soluble (170° C.)	Insoluble in tung oil
Durez 500	Soluble (70° C.)	
Glyptal #1231	Soluble (160° C.)	
Run congo gum	Soluble (170° C.)	
Durez 4758	Soluble (80° C.)	
Lewisol #2	Soluble (150° C.)	
Varcum 250	Soluble (120° C.)	

(3) Water Permeability - Water resistance tests on standard varnishes indicate that index oil varnishes, turn white in water very much more slowly than linseed oil varnishes. However, on drying, varnishes containing this oil return quickly to the transparent condition, and show no after effects in strength or durability of the film.

The following varnishes were made as a means of comparing index, linseed and tung oil:

No. 1 100 gr. ester gum
100 gr. Index oil
0.02% cobalt oilsalate
200 gr. turpentine

No. 2 100 gr. ester gum
100 gr. Tung oil
0.01% cobalt oilsalate
200 gr. turpentine

No. 3 100 gr. ester gum
150 gr. Index oil
0.02% cobalt oilsalate
200 gr. turpentine

No. 4 100 gr. ester gum
100 gr. Superb linseed oil
0.02% cobalt oilsalate
200 gr. turpentine

The procedure was the same for all. The ester gum and oil were mixed and heated to 560° F. until the varnish had a good body. It was then cooled to 300° F. and the turpentine was added; the drier was then added and the varnish filtered through cloth. The time of bodying at 560° F., for the different varnishes, to get approximately the same consistency, was:

No. 1	3/4 hour
No. 2	5 minutes
No. 3	1½ hours
No. 4	2 hours (not bodied as much as others)

The water resistance of films made from these varnishes was tested in two ways:

(a) Immersion in water at room temperature for 8 days, and

(b) Immersion in boiling water for one hour.

In each case, films were flowed on metal strips, which were immersed 2½ inches into the water. The films were examined immediately after removal and also several days later. The results are as follows:

TABLE XXVII.

Resistance to Water at Room Temperature

Varnish Number	Immediate		After 8 Days	
	Appearance	Softening	Appearance	Loss of Gloss
1	Muddy	Slight	O.K.	O.K.
2	Very little change	Very slight	O.K.	O.K.
3	Muddy	Slight	O.K.	O.K.
4	White	Great	White	Very much

TABLE XXVIII.

Resistance to Boiling Water For One Hour

Varnish Number	Appearance After 2 Days	Relative Value
1	Pitted, scaly, white	3
2	White	2
3	Muddy	1
4	Pitted, scaly, white	3

These varnishes were also tested by bending metal strips on which films had been flowed and dried, around 3/32" tubing. No cracks appeared in any of the films.

A mixture of 50% index oil and 50% tung oil produced a finished varnish in practically the same time as pure tung oil. The quality of the finished product was also equal to that produced with straight tung oil. Mixtures up to two-thirds index oil to one-third tung oil produced comparatively waterproof varnishes, but 100% index oil varnishes were not equivalent to tung oil varnishes in color and waterproofness. In these mixtures, the index oil and tung oil may be mixed before cooking, or some of the index oil may be withheld to control the "cook". The index oil may also be used as a cold blending oil. Any one of these blending methods may be used without impairing the qualities of the final product.

(4) <u>Drier Precipitation</u> - Manganese and cobalt driers can be added to all index oils in the cold without any deliterious effects. However, lead, as Nuodex, oilsolate, linoleate or resinate, precipitates from index oils. Lead tungate remains in linseed index oil, but is thrown out of soybean index oil immediately upon addition. If mixtures of lead and either cobalt or manganese driers were used, both metallic salts precipitated. In every case, the precipitation was roughly proportional to the

amount of lead drier.

Untreated oils exhibit similar but less marked effects.

This precipitation is probably due to ester interchange leading to insoluble soaps of the metal. Krumbhaar (471) agrees with this theory and adds another possibility, namely, the action of driers on hydroxyl groups in the oil. Droste (472) states that the decomposition reactions of oxidizing oils result in free acids which form salts with metallic pigments; the same is probably true for metallic driers.

(5) Artificial Gelation with $FeCl_3$ - The preparation of brake lining saturants is sometimes made by adding a solution of $FeCl_3$ in acetone to tung oil. If straight tung oil is used, the gelation is very rapid, and the product formed is dry and crumbly. If the tung oil is dissolved in benzene before the ferric chloride solution is added, gelation is greatly inhibited.

In order to see if a similar reaction might not take place with index oil, three different catalysts were added in various quantities to 40 point Superb linseed index oil. The catalysts were a chloroform solution of anhydrous $SnCl_4$ (17.2 g. $SnCl_4$ to 60.5 g. $CHCl_3$), a nearly saturated solution of $FeCl_3.6H_2O$ in acetone, and an acetone solution of $SnCl_4.5H_2O$ (40 g. $SnCl_4.5H_2O$ in 60 cc. of solution). The procedure followed was to dissolve the index oil in various solvents (1 to 1), and add the solutions of catalysts both individually and mixed. Since none of the samples gelled at room temperature, all of the samples were poured on watch crystals and placed in the oven at 85° C.

Nearly 100 different mixtures were tried with varying success. The following are typical. All samples consist of 15 cc. of the index oil and 14 cc. of benzene, plus the following:

(1) 1 cc. $FeCl_3$ solution. This produced a smooth tough skin over a black viscous liquid.

(2) 0.1 cc. $FeCl_3$ solution. This produced a clear reddish gel with a thin wrinkled skin.

(3) 1 cc. anhydrous $SnCl_4$ solution. This produced a black, slightly sticky gel with no skin effect.

(4) 0.1 cc. anhydrous $SnCl_4$ solution. This produced a viscous solution, very like the original oil.

(5) 1 cc. of $SnCl_4.5H_2O$ solution. A black gel not as sticky as (3).

(6) 0.1 cc. $SnCl_4.5H_2O$ solution. This yielded a very viscous oil, slightly darker than the original.

(7) 0.4 cc. of $FeCl_3$ solution and 0.1 cc. of $SnCl_4.5H_2O$ solution. This yielded a cloudy brownish liquid of the consistency of the original oil.

(8) 0.1 cc. $FeCl_3$ solution and 0.4 cc. of $SnCl_4.5H_2O$ solution. This formed a sticky, slightly moist gel covered with a strong smooth skin.

(9) 0.4 cc. $FeCl_3$ solution and 0.1 cc. of anhydrous $SnCl_4$ solution. This yielded a very sticky wet gel covered with a medium strong, slightly wrinkled skin.

(10) 0.1 cc. $FeCl_3$ solution with 0.4 cc. solution of anhydrous $SnCl_4$. This produced a sticky, clear, strong gel covered with a tough wrinkled skin.

(11) 0.5 cc. $FeCl_3$ solution. This mixture gelled and was covered with a tough, hard, wrinkled skin.

(12) 0.5 cc. anhydrous $SnCl_4$ solution. This produced a good gel with no skin.

(13) 0.5 cc. $SnCl_4.5H_2O$. This formed a very viscous semi-gelled liquid with a slight skin effect.

In all cases the gels produced were much more plastic and cohesive than gels produced in a similar manner from tung oil. It will be noted that 1 cc. of $FeCl_3$ solution did not produce a gel, although 0.1 cc. did. With tung oil there appears to be no limit to the amount of $FeCl_3$ solution that may be used to produce a gel. The more that is added, the more quickly the gel forms. $FeCl_3$ always produces a skin over the index oil when it gels it. No skin effect was noted with tung oil. Stannic chloride catalyst in contra-distinction to the $FeCl_3$, reacted more rapidly with increasing concentration. Furthermore, with stannic chloride no skin effect was observed.

It was thought that a mixture of the two catalysts might serve to produce a gel with no skin. It was with this in mind that tests 7, 8, 9 and 10 were carried out. The results were not favorable. The two catalysts seemed to have a mutual inhibiting effect, so that quantities of $FeCl_3$, which by themselves would have been sufficient to produce good gels, produced sticky wet gels or viscous liquids when the $SnCl_4$ was added. Furthermore, even these sticky gels were covered with skins.

A set of samples was made up, using 30 cc. of the index oil and 28 cc. of benzene. One-tenth cc. of $FeCl_3$ was found to be sufficient to gel these if no stannic chloride was added. It was found that the samples could be gelled even though stannic chloride was added, if the temperature of the oven was raised to 150° C. instead of 85° C. Addition of moderate quantities of $FeCl_3$ solution to the index oil resulted in the evolution of considerable heat. These results are all very interesting, inasmuch as no gels could be produced in this manner using untreated Superb linseed oil.

(6) <u>Heat Bodying</u> - When an index oil is heat bodied in air, an exothermic reaction takes place, the oil foams badly, and the color changes from a light yellow to a

dark reddish brown. Further heating up to 300° C. causes a slight darkening of this color. When heated at 300° C. for one hour, the oil gels. Untreated linseed oil, when subjected to the same heating procedure, undergoes no change in color. The bodying process proceeds smoothly, and no excessive foaming occurs at any time. However, the time for the formation of a gel is about 8 hours. The index oil bodies in a much shorter time (one hour), and is comparable to tung oil in this respect.

The effect of hydroquinone on the coloration of index oil was observed by heating a 49 point Superb linseed index oil with 0.1% hydroquinone. A slight reduction in color incurred, but the final color was still definitely reddish. Aminophenols, triamylamines, and carbon decolorizers may prove of some value in this respect.

Pressure does not inhibit these color-forming reactions because a sample of an index oil colored even when bodied in an autoclave under nitrogen pressure.

The change in refractive index when an index oil is heated to 200° C. in less than five minutes was found to average 15 points increase for oils which had an initial index of 30 or more. Even oils which were only slightly oxidized, showed some increase in index upon heating. These preliminary results are tabulated in the following table:

TABLE XXIX.

Run Number	Initial Index	Final Index	Change, In Index
21a	29	48	19
22b	35	58	23
23a	40	53	13
24a	45	60	15
25a	39	53	14
26c	2	8	6
28e	50	68	18
29e	40	55	15
30e	35	46	11
31d	11	18	7
32d	2	3	1
100	0	4	4

~~A more extensive~~ investigation of the property changes which occur during the bodying of an index oil was made as a result of these preliminary tests. A 40 point Superb linseed index oil was heat bodied in a large iron pot and 100 cc. samples were taken at frequent intervals. The results of this test are summarized in Table XXX. ~~and are graphically portrayed in Figures 43 to 49 inclusive.~~

As a means of comparison, a sample of the original Superb linseed oil was also bodied under similar conditions. The results of this test are summarized in Table XXXI., ~~and are graphically plotted for comparison in Figures 43 to 49 inclusive.~~ The results on molecular weight are due to Wentz (473).

TABLE XXX.

Heat Bodying of Index Oil

Sample Number	Elapsed Time, Minutes	Temperature °C.	Refractive Index at 25° C.	Specific Gravity	Absolute Viscosity	Molecular Weight	Iodine Number	Acid Value
1	0	20	1.4752	0.9571	1.727	1172	126.7	2.59
2	8.5	50	1.4753	0.9579	1.730	1156	128.4	2.81
3	18.5	85	1.4751	0.9576	1.785	1152	128.0	2.83
4	26.5	120	1.4751	0.9576	2.080	1130	127.3	3.83
5	31	150	1.4749	0.9581	2.314	1127	128.1	6.06
6	32	160	1.4746	0.9583	2.337	1146	126.0	5.55
7	33	170	1.4753	0.9575	2.399	1154	123.4	5.29
8	39	180	1.4760	0.9575	2.418	1164	119.8	3.56
9	48	195	1.4763	0.9577	2.575	1209	118.4	2.95
10	53	205	1.4769	0.9580	2.749	1230	111.7	2.71
11	61	220	1.4771	0.9582	2.713	1226	117.3	2.65
12	66.5	225	1.4774	0.9590	2.820	1243	118.5	2.51
13	76	235	1.4779	0.9594	3.110	1266	118.0	2.68
14	83	245	1.4779	0.9595	-----	1289	118.3	2.63
15	91.5	262	1.4783	0.9612	-----	1314	116.5	2.87
16	98	275	1.4790	0.9624	-----	1342	114.9	3.26
17	104.5	285	1.4795	0.9644	-----	1425	109.7	3.67
18	115.5	293	1.4806	0.9699	13.385	1542	100.7	4.41
19	125.5	293	1.4819	0.9767	-----	1774	97.8	4.39
20	140.5	293	1.4840	0.9810	-----	----	84.1	6.41
21	154	293	1.4848	------	-----	----	82.6	----
22	164	293	Gelled	------	-----	----	----	----

TABLE XXXI.

Heat Bodying of Superb Linseed Oil

Sample Number	Elapsed Time, Minutes	Temperature °C.	Refractive Index at 25° C.	Specific Gravity	Absolute Viscosity	Iodine Number	Acid Value
1	0	25	1.4711	0.9291	0.395	167.5	0.41
2	14	110	1.4708	0.9292	0.400	167.0	0.44
3	30	200	1.4713	0.9293	0.408	165.0	0.42
4	70	293	1.4721	0.9316	0.536	163.2	0.81
5	100	293	1.4731	0.9345	0.820	153.2	1.20
6	130	293	1.4744	0.9387	1.280	144.7	1.63
7	160	293	1.4753	0.9424	2.069	137.7	1.99
8	190	293	1.4764	0.9464	3.017	132.9	2.32
9	220	293	1.4776	0.9472	5.365	125.5	2.60
10	250	293	1.4785	0.9532	8.194	122.2	2.88
11	280	293	1.4793	0.9568	10.321	118.1	3.15
12	310	293	1.4798	0.9592	17.331	117.2	3.30
13	340	293	1.4808	0.9583	22.203	110.9	3.62
14	370	293	1.4812	0.9657	55.334	108.1	3.87
15	400	293	1.4818	0.9683	78.432	106.1	4.10
16	430	293	1.4830	------	------	101.1	4.54
17	460	293	1.4834	------	------	97.4	5.15
18	473	293	Gelled	------	------	----	----

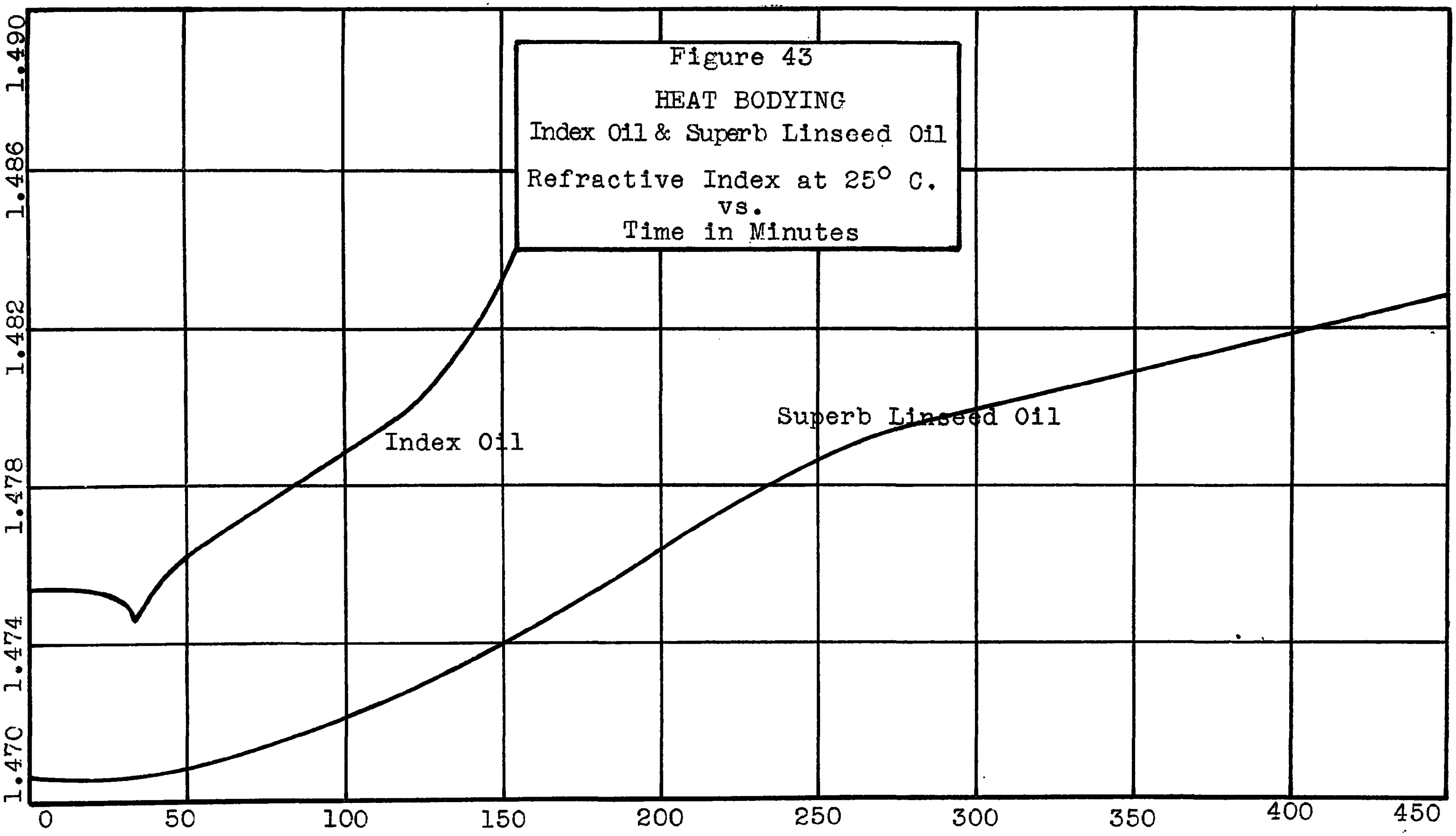


Figure 43

HEAT BODYING

Index Oil & Superb Linseed Oil

Refractive Index at 25° C.
vs.
Time in Minutes

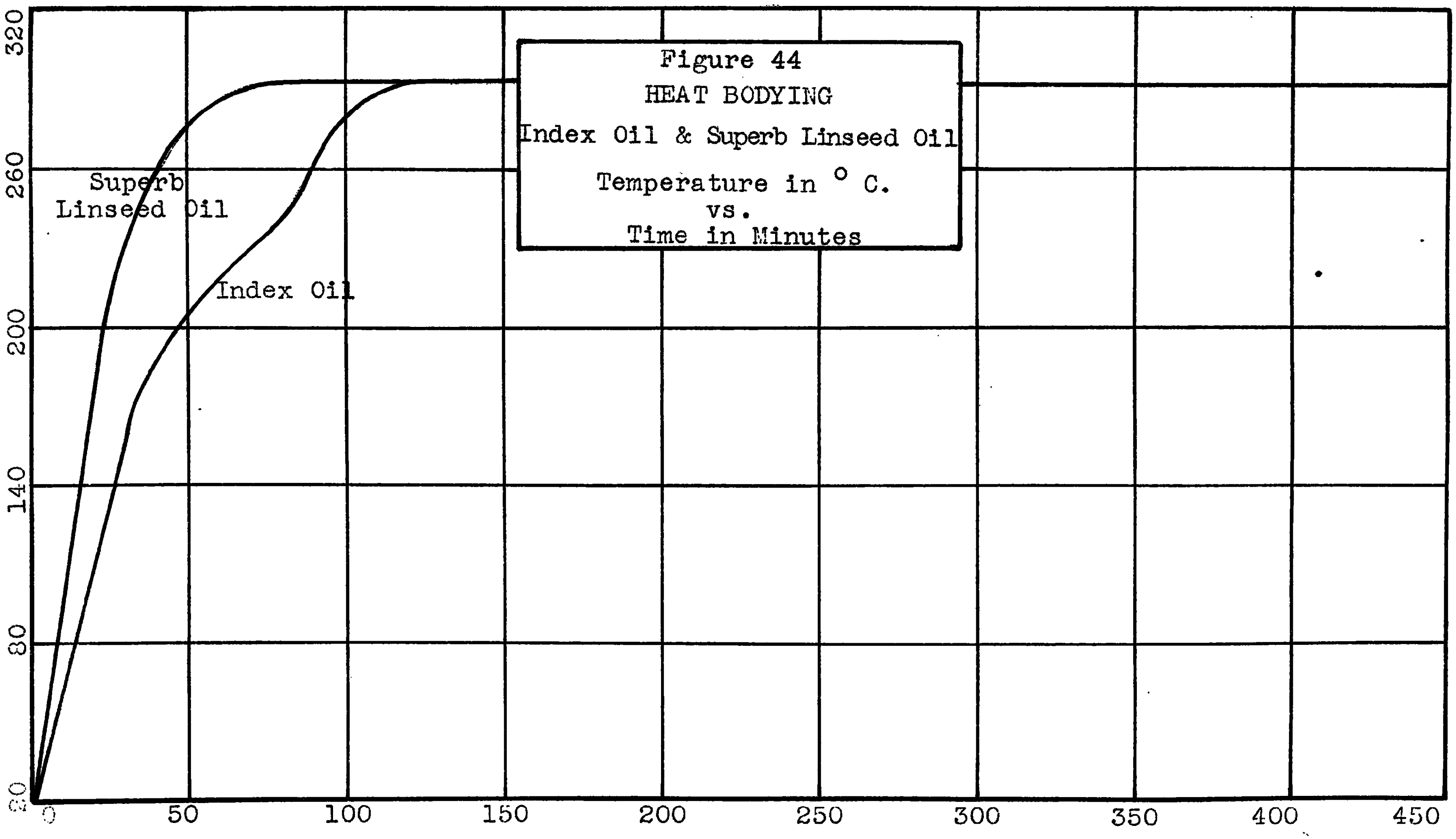


Figure 44
HEAT BODYING
Index Oil & Superb Linseed Oil
Temperature in ° C.
vs.
Time in Minutes

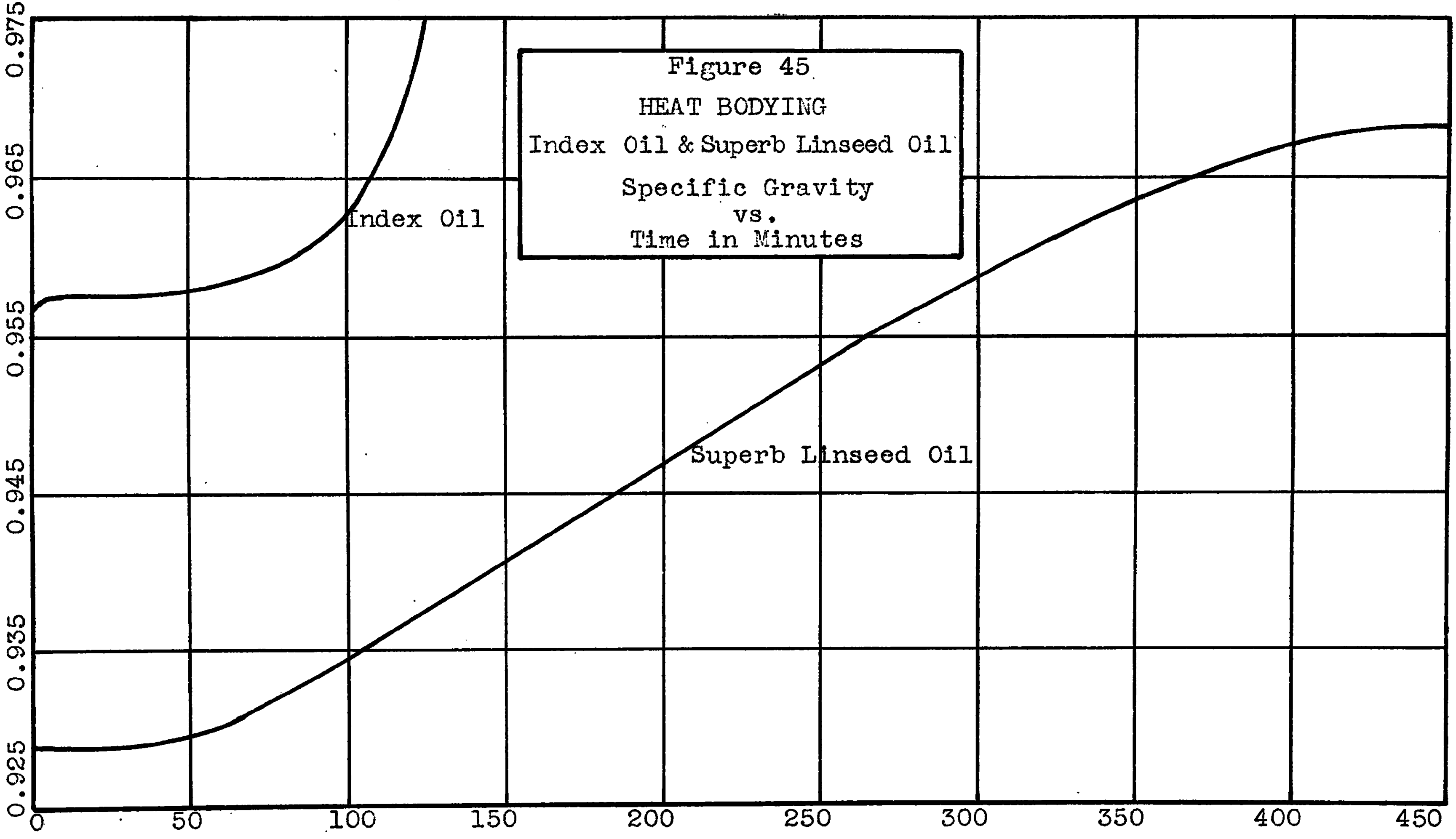


Figure 45

HEAT BODYING

Index Oil & Superb Linseed Oil

Specific Gravity
vs.
Time in Minutes

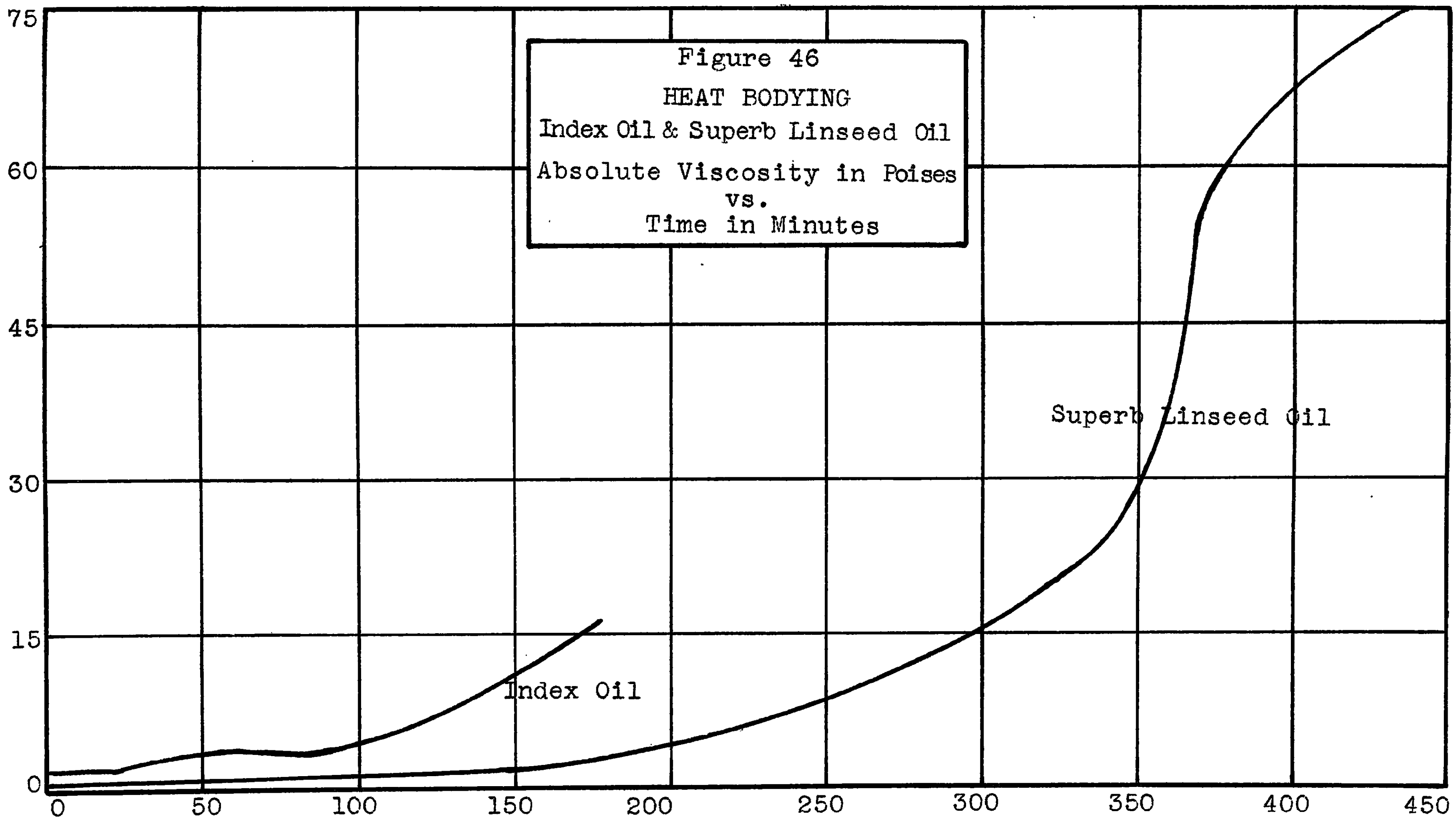


Figure 46

HEAT BODYING

Index Oil & Superb Linseed Oil

Absolute Viscosity in Poises
vs.
Time in Minutes

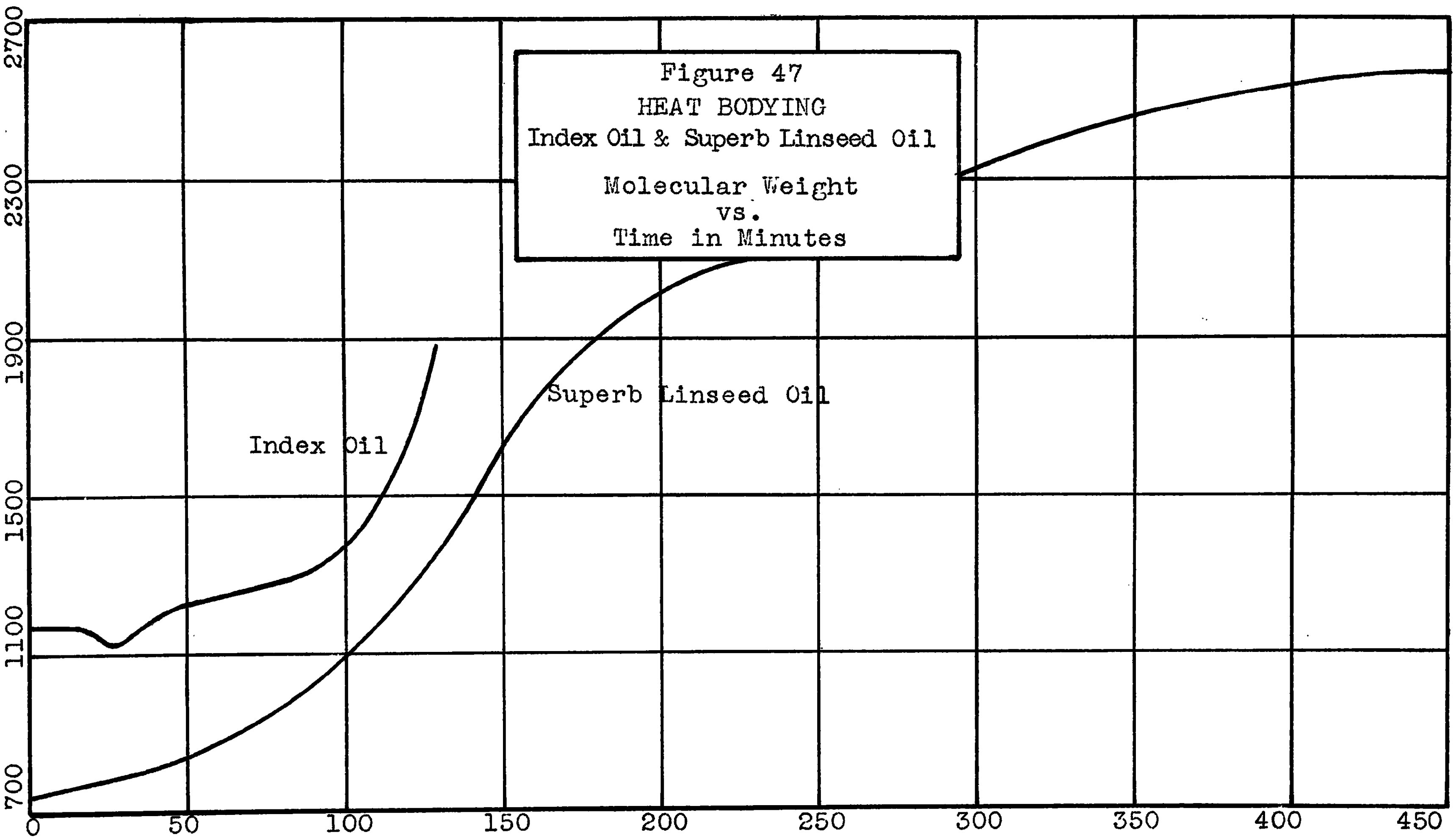


Figure 47
HEAT BODYING
Index Oil & Superb Linseed Oil

Molecular Weight
vs.
Time in Minutes

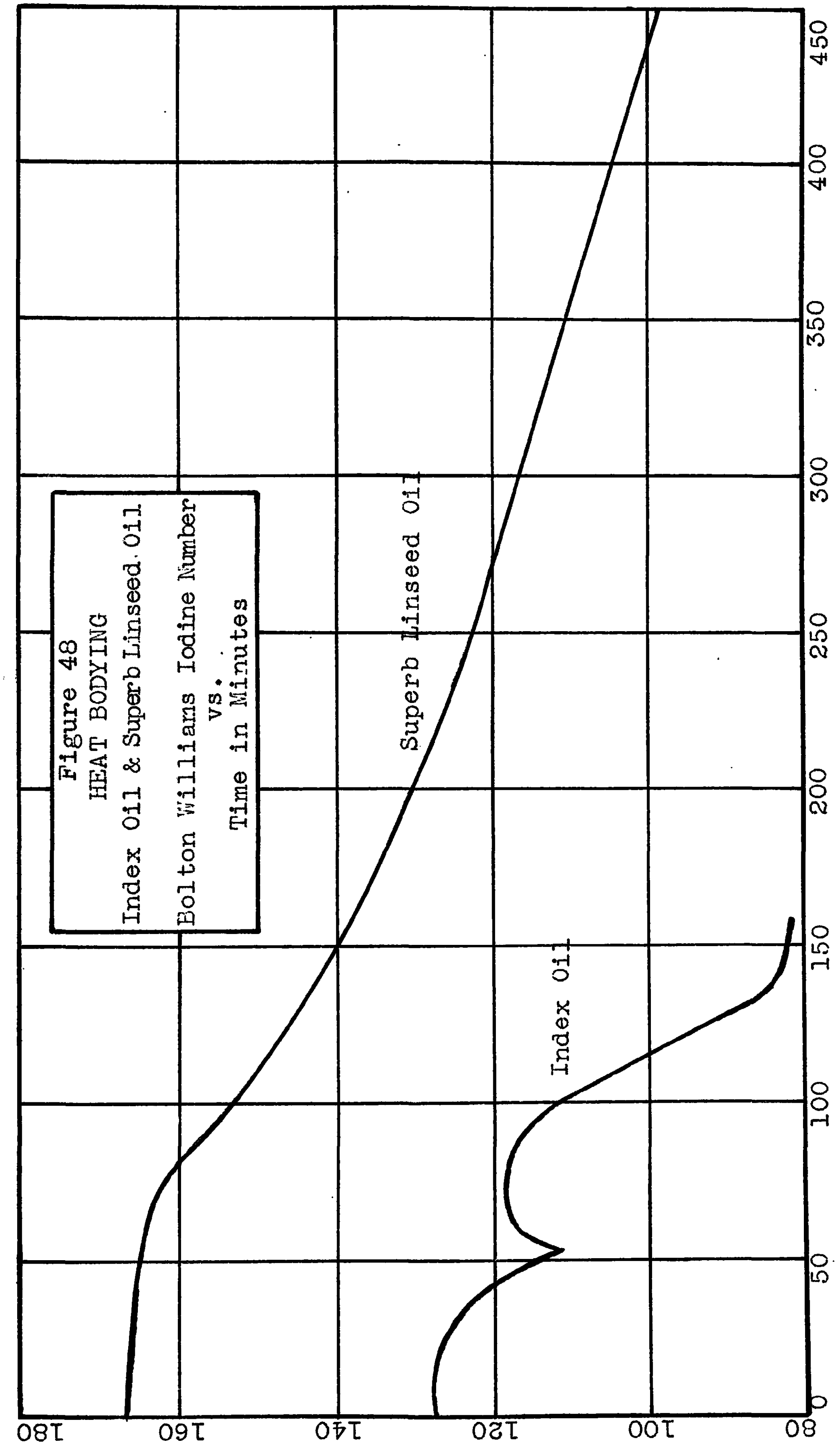


Figure 48
HEAT BODYING
Index Oil & Superb Linseed Oil
Bolton Williams Iodine Number
vs.
Time in Minutes

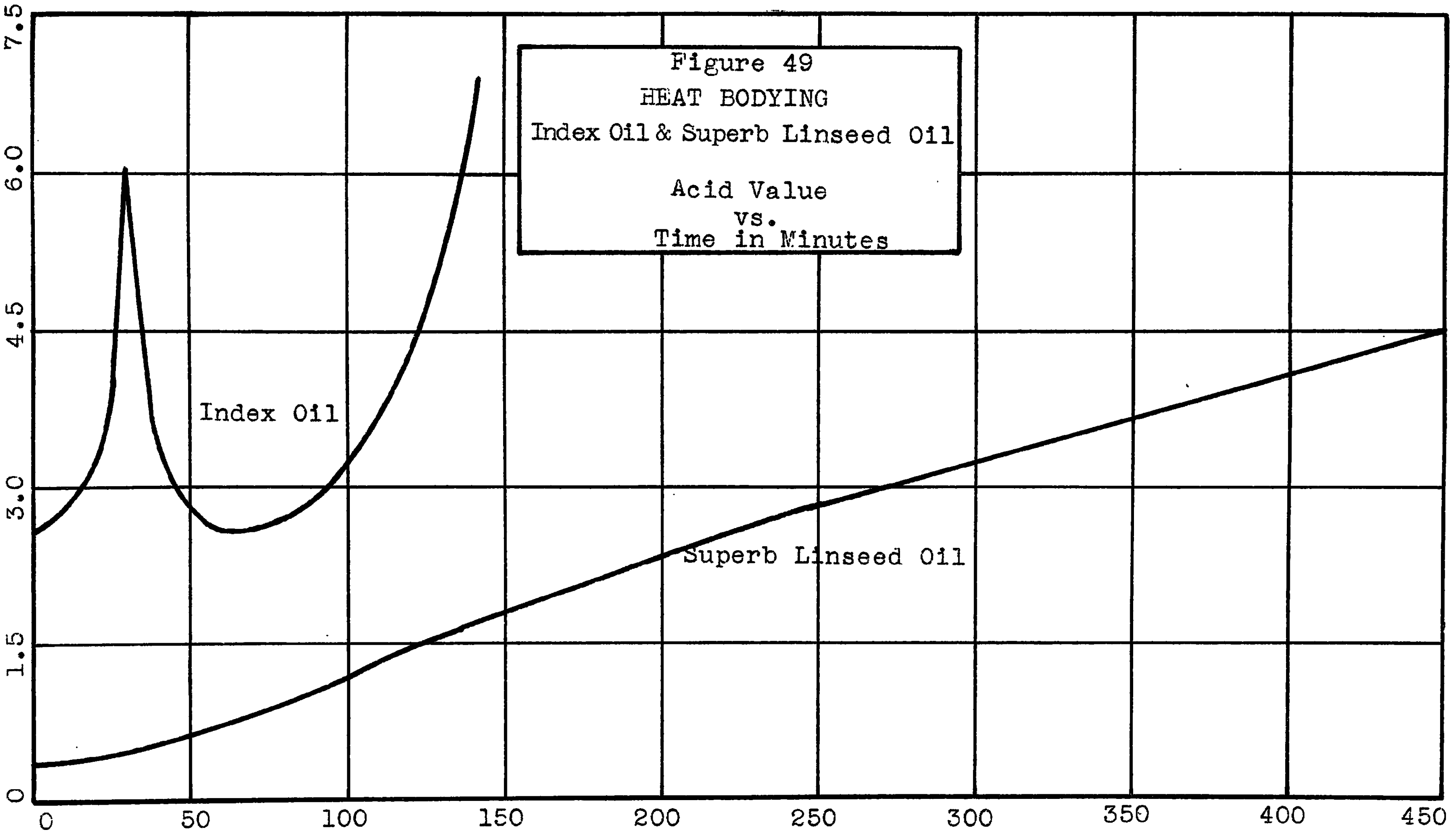


Figure 49
HEAT BODYING
Index Oil & Superb Linseed Oil

Acid Value
vs.
Time in Minutes

There are two fundamental differences between these two sets of curves. In the bodying of the index oil, the gelation time is much shorter than that of Superb linseed oil; furthermore, in the bodying of index oil there are definite maxima and minima in iodine number, acid value, refractive index and molecular weight, whereas these properties change smoothly in the bodying of Superb linseed oil. The theoretical significance of these observations will be discussed in a later section.

During the heat bodying of index oils, the evolution of large volumes of gas was noticed. Numerous tests were made on these gaseous products, but the results are difficult to analyze because of the complexity of the material and the probable variety of these gaseous constituents.

In the first of these runs, 100 grams of index oil 60k were heated up to 200° C., and the gaseous products were passed successively over dehydrite (anhyd. $MgClO_4$), ascarite (NaOH asbestos), and copper gauze. Nitrogen was continuously passed through the apparatus, which included an air condenser, a distillation flask trap, and a gas wash bottle trap, preceding the gas absorption train.

During the run, the copper gauze turned black below 110° C. and then became brighter after 140° C. An acrid odor, predominantly acrylic, was noticed during the run;

at temperatures over 130° C. the oil underwent decomposition reactions which produced loud noises. At the end of the run an unidentified quantity of liquid was present in the distilling flask; this liquid had a strong odor, was turbid and yellow-white in color, and contained definite amounts of water. This distillate was placed in a sealed bottle and allowed to age. Several weeks later only a reddish-brown solid remained in the bottle; evidently the organic material had polymerized to a resin.

The results from the absorption train show 0.52% water and/or fatty acids and 0.07% CO_2. The copper gauze lost 0.04 grams, but since several opposing forces were influencing this absorber, these results are meaningless. The dehydrite absorption is low because of condensation of both water and acids previous to the dehydrite absorption bottle. The CO_2 determination is probably definite and significant.

In run 65 and in all subsequent runs, use was made of a commercially blown batch of SH'd linseed oil. This oil, RB16, had been blown 47 points, and had a pipette viscosity of 40 seconds at 86° F. The set-up for this run was slightly different from that of run 60kh; the gas wash bottle was half filled with ether, and two dehydrite absorbers were connected in series immediately following the ether absorber. The ascarite, copper gauze, and distillate trap occupied their normal positions. The data for this run is reproduced in Table XXXII.

TABLE XXXII.

Critical Period Heating of Index Oil RB16

Elapsed Time in Minutes	Temperature in ° C.	Remarks
0	21	N_2 slowly being passed through.
7	50	Cu gauze is black.
11	75	Definite gas evolution.
15	97	
19	104	
24	103	
25	108	Cu gauze still black.
29	114	
32	116	Slight foaming.
37	118	More foaming.
50	120	Slight color.
55	128	Foam, Cu black, Roasted almond smell, no distillate.
65	134	Cu gauze, not as black.
71	139	Cu much brighter.
75	138	Cu gauze is bright.
84	141	Droplets on end of Cu absorber.
90	141	
94	140	
101	145	
107	148	
115	147	Slight fog at top of condenser.
125	156	Oil color darker; less foaming.
140	164	More fog on condenser tubes.
147	164	Oil is very dark.
155	165	
165	168	Cu gauze has a dirty color.
175	172	Fog at condenser.
179	177	
185	191	
187	204	
198	210	Some foaming, bubble crackling.
200	216	
201	220	Heat off.
204	181	
208	157	Still slight bubbling.

Per cent CO_2 = 0.12%

The dehydrite and copper gauze absorbers gave meaningless results; the dehydrite absorbed some of the ether, and the copper gauze had no selective absorption for any one constituent. The CO_2 determination checks previous work and has definite significance.

In the following runs, the gas samples obtained by heating RB16 index oil were analyzed by the standard Orsat methods. The following absorption pipettes were successively used:

(a) 33% KOH to remove CO_2 and fatty acids
(b) Fuming H_2SO_4 to remove unsaturates
(c) Alkaline pyrogallol to remove oxygen
(d) Ammoniacal Cu_2Cl_2 to remove CO
(e) CuO at 220° C. to remove H_2

The residual gas was, in most cases, burned in oxygen and subsequently tested for the CO_2 and H_2O formed during the combustion. This combustion is essentially to remove hydrocarbons, but other organic substances seem to be involved in both the CuO reaction and this combustion reaction.

A series of three heats was made on RB16 index oil, and numerous samples were analyzed from each of these runs. Considerable difficulty was experienced in obtaining duplicate results because of the variable absorptions of the myriad of substances which appear to be present in the evolved gases. No calculations could be made on the combustion data because of the complexity of the sample; in fact, a residue, which was greater than the nitrogen known to be present, was always left after the excess oxygen was absorbed. The percentage value indicated by the CuO tube was very erratic because substances other than hydrogen were being oxidized by this reagent.

The results of most of these runs are summarized in Table XXXIII.

In this table the following facts are to be noted:

(a) The indicated percentage of CO_2 actually includes any acid vapors in the gas. However, these will be extremely small since the water in the Orsat apparatus will absorb the greater portion of the acids.

(b) The indicated percentage of H_2 actually includes unknown substances, probably aldehydes, which react with CuO at 220° C.

(c) The indicated percentage of CO_2 produced refers to gases which react with CuO to form CO_2, and includes any CO in the original gas if this particular constituent has not been previously removed. The average figures are always based on CO_2 produced from substances other than CO.

(d) Runs with three-number designations are straight combustions.

TABLE XXXIII.

Analysis of Gases From The Heating of RB16 Index Oil

Run Number	Heating Range	Diluent Gas	% CO_2[a]	% Unsaturates	% Oxygen	% CO
90-1	20°-142°C.	N_2	1.46	0.00	3.67	----
91-1	142°-151°C.	"	3.00	0.15	3.53	----
91-2	"	"	2.58	----	2.87	----
91-3	"	"	2.19	----	3.10	----
91-4	"	"	----	----	----	----
92-1	20°-205° C.	"	3.98	0.48	2.17	----
92-2	"	"	3.63	0.33	3.46	----
92-2'	"	"	3.60	0.33	2.42	----
92-3	"	"	3.52	0.29	3.46	----
92-3-1	"	"	----	----	----	----
92-3-2	"	"	----	----	----	----
92-3-3	"	"	----	----	----	----
92-3-4	"	"	----	----	----	----
92-3-5	"	"	----	----	----	----
92-4	"	"	3.15	2.42	7.08	----
92-5	"	"	3.33	3.10	3.91	----
92-6	"	"	3.62	0.22	2.41	----
92-7	"	"	3.58	0.30	2.39	1.19
92-7-1	"	"	----	----	----	----
92-A	"	"	3.6	0.3	2.4	1.2
92-A-1	"	"	----	----	----	----
93-1	24°-205°C.	CO_2	64.86	0.61	3.05	----
93-2	"	"	60.25	0.42	4.49	----
93-2-1	"	"	53.60	----	----	----
93-3	"	"	58.85	0.34	5.76	3.19
93-3-1	"	"	55.70	----	----	----
93-A	"	"	60.0	0.45	4.4	3.2
93-A-1	"	"	54.6	----	----	----

TABLE XXXIII.

(continued)

			Combustion Analysis			
Run Number	% Hydrogen[b]	$\%CO_2$ Produced[c]	% Decrease	$\% CO_2$	$\%O_2$ Consumed	% Residual
90-1	10.27	0.00	----	----	----	84.6
91-1	26.70	0.90	----	----	----	65.7
91-2	17.75	1.09	----	----	----	75.7
91-3	19.22	1.27	----	----	----	74.2
91-4	-----	----	37.8	12.0	----	----
92-1	13.87	1.33	12.5	----	----	----
92-2	9.84	0.77	9.2	----	----	----
92-2'	13.66	1.11	9.0	6.3	----	----
92-3	12.00	1.90	8.7	5.6	----	----
92-3-1	-----	----	33.0	11.5	----	----
92-3-2	-----	----	22.6	11.5	----	----
92-3-3	-----	----	21.9	11.7	----	----
92-3-4	-----	----	22.2	12.4	----	----
92-3-5	-----	----	21.3	11.6	----	----
92-4	10.05	2.00	3.3	4.1	----	----
92-5	10.40	1.84	5.9	7.3	----	----
92-6	10.58	2.30	9.0	5.6	25.8	88.8
92-7	10.68	1.37	7.1	4.5	29.0	90.7
92-7-1	-----	----	21.0	10.8	38.0	100.6
92-A	11.4	1.4	9.0	5.5	27.7	89.7
92-A-1	----	---	21.8	11.6	38.0	100.6
93-1	16.09	2.92	3.2	1.9	10.8	13.6
93-2	12.85	3.18	8.1	6.4	14.0	18.5
93-2-1	-----	----	31.3	13.3	17.3	18.6
93-3	13.36	1.02	7.1	5.6	11.6	15.5
93-3-1	-----	----	30.2	13.0	17.4	18.5
93-A	13.1	1.0	7.5	6.0	12.3	18.5
93-A-1	----	---	30.7	13.2	17.3	18.5

(e) Average percentages, indicated by A, are based on weighted analysis of the various runs.

(f) The combustion results are calculated to percentages of the original sample; specific gas calculations are impossible.

Although the quantitative significance of these runs is in some doubt, there is no question as to their qualitative indications. The oxidation and decomposition reactions which occur during this heating process, produce definite quantities of CO_2, CO, O_2, H_2, aldehydes, unsaturates and hydrocarbons.

An attempt was made to correlate the ratio of volume decrease to CO_2 to O_2 consumed with the theoretical ratios of numerous organic hydrocarbons, acids, aldehydes, ketones, hydroxyacids, ketonic acids, olefins, diolefins, unsaturated aldehydes and acids, and alcohols. No simple explanation of the observed results could be obtained; the oxygen consumption is abnormally high, and the residual gas usually had a larger volume than the original sample. In other words, organic compounds were burning in the combustion pipette and producing multivolume products which were stable to further combustion.

Since the decrease was always greater than the CO_2 produced, methane must be one of the gaseous constituents. The large oxygen consumption indicates higher hydrocarbons and unsaturated aldehydes and acids. These latter may be produced in the copper oxide tube, and further oxidized in the combustion pipette.

The total combustion results definitely show the presence of hydrogen gas because the percentage decrease is abnormally high, compared with runs in which the hydrogen constituent had been removed.

In run 93, there was a combustion residue in every case, although no nitrogen is present in the gaseous mixture.

In runs 92-2' and 92-3, the combustion results were calculated to methane, ethane and nitrogen. The percentages were then expressed on the basis of (a) total sample, and (b) gases from the oil. These calculations are as follows:

TABLE XXXIV.

Gas Analysis	Run 92-2'		Run 92-3	
	(a)	(b)	(a)	(b)
% CO_2	3.60	14.40	3.52	14.02
% Unsaturates	0.33	1.32	0.29	1.15
% O_2	2.42	9.68	3.46	13.80
% H_2	13.66	54.60	12.00	47.80
% CO	1.11	4.44	1.90	7.57
% CH_4	1.57	6.28	2.21	8.80
% C_2H_6	2.36	9.84	1.70	6.77
% N_2	75.00	----	74.90	----

When viewed from the point of gases from the oil, the quantities of CO_2, O_2 and H_2 are quite large.

In an attempt to correlate the total combustion analysis with the absorption-combustion analysis, it was assumed that the copper oxide analyzed only for hydrogen and carbon monoxide, and that the unsaturates corresponded generally to ethylene. On this basis, the percent decrease and the percent CO_2 were compared for both types of analysis. The agreement is better than expected, as shown by the following tables:

TABLE XXXV.

Correlation of Analytical Data

Run Number	% Decrease of Unabsorbed	% Decrease of Absorbed	Total % Decrease	Experimental Total Decrease	Run Number
92-1	12.55	22.33	34.9	33.0	92-3-1
92-2	9.21	15.97	25.2	22.6	92-3-2
92-2'	9.02	21.54	30.6	21.9	92-3-3
92-3	8.70	19.63	28.3	22.2	92-3-4
92-6	8.98	18.61	27.6	21.7	92-3-5
92-A	9.0	19.0	28.0	21.8	92-A-1

TABLE XXXVI.

Correlation of Analytical Data

Run Number	% CO_2 of Unabsorbed	% CO_2 of Absorbed	Total % CO_2	Experimental Total CO_2	Run Number
92-2'	6.28	5.37	11.65	11.52	92-3-1
92-3	5.61	6.00	11.61	11.54	92-3-2
92-6	5.62	6.36	11.98	11.67	92-3-3
92-1	----	6.27	-----	11.60	92-3-5
92-A	5.5	6.2	11.7	11.6	92-A-1

Since aldehydes, acids, etc. are probably in the gases from heated index oil, low temperatures should condense most of these compounds. Only hydrocarbons such as methane, ethylene, etc. can remain gaseous at temperatures around-80° C. A quantity of gas was prepared in run 94, using nitrogen diluent. An Erlenmeyer flask, containing a vacuum stopcock, was evacuated to less than 10 mm. Hg. A sample of the gas was drawn into the flask, and the entire mass was cooled in an acetone-dry ice bath. Pressure and temperature readings were taken at definite intervals of time. The results of these tests were corrected for the water content of the gas sample, assuming that the gas was saturated at room temperature. A sample calculation is as follows:

(1) Pressure of 8.50 in. Hg at 24° C.

(2) Pressure of $^{-}3.25$ in. Hg at -78.7° C.

(3) Total volume of gas = 530 cc.

(4) Vapor pressure of water at 24° C.=22.18 mm. Hg

(5) Water content = 22.18/760 x 530 = 15.4 cc.

(6) Pressure change due to cooling =

$$760 - \frac{194.3}{297} \times 760 = 266 \text{ mm. Hg}$$

(7) Actual pressure change = 11.75 x 25.4 = 298.5 mm. Hg

(8) Difference in pressure due to condensation = 32.5 mm. Hg

(9) Volume of sample condensed = $\frac{32.5}{760} \times 530 = 23$ cc.

(10) Volume of condensate in the gas from the oil = 7.6 cc.

Several other runs were made, but difficulty was found in estimating the true gas temperature; one result actually came out negative when corrected for the saturated water content. Two runs gave fairly close checks; the results in these cases were 57 cc. and 53.5 cc. of condensate respectively. The run for which the calculation is shown, gives low results because the gas mixture was not actually at-78.7° C. Since the flask was incompletely filled with the gases from the heating of index oil, the actual percentage of condensibles approximates 12 per cent.

An analysis was made of this gas with the following results:

CO_2 = 2.9%
Unsaturates = 3.7%
O_2 = 3.9%
CO = 0.9%
H_2 = 8.2%
CO_2 (produced) = 0.0%
Decrease (combustion) = 7.9%
CO_2 (combustion) = 6.9%
O_2 consumed = 6.1%
Residue = 71.9%

The presence of aldehydes in these gases was qualitatively shown by their reaction with saturated $NaHSO_3$.

The amounts of acids produced on heating index oil RB16 were determined by successively passing the gases through absorption bottles containing ether, acetone and water, and water, respectively. These solutions were titrated with 0.0945 N alcoholic KOH; the results were then corrected for the blank determinations on the absorbing liquids. The following data was obtained:

weight of oil = 453.6 g.
blank titration = 1.4 cc. 0.0945 N KOH
sample titration = 198 cc. 0.0945 N KOH

from which we can calculate

0.036 moles acids/mole oil

In a final attempt to clarify the complex nature of these gaseous products, run 94 was made, in which samples were withdrawn over definite temperature periods, and analyzed to determine what reactions might be occurring at certain stages in this critical period of index oil bodying. The data on this run is shown in the following table:

TABLE XXXVII.

Critical Period Heating of RB16 Index Oil

Weight of Oil = 428.3 g.
Diluent gas = Nitrogen

Time in Minutes	Temperature in ° C.	Remarks
--	26	Nitrogen going in.
0	26	Nitrogen off.
7	110	
11	115	Sample 94-1.
14	140	
17	145	White fumes; color darker.
19	146	Sample 94-2.
22	146	Very much gas; exothermic.
25	162	
36	177	Sample 94-3.
40	195	Strong reaction, but very little gas.
45	210	
51	225	Sample 94-4.
51	225	Nitrogen going in.
52	220	Sample 94-5.
54	220	Sample 94-6.
55	220	Sample 94-7.

Careful analyses of these samples were made, and the results were calculated to volumes. To do this, it was assumed that the nitrogen diluent was completely removed in the first two samples, and that the residues in samples 1, 5, 6 and 7 were all nitrogen gas. The validity of these assumptions is upheld by the combustion results; when the per cent decrease and the per cent CO_2 from the combustion reactions are both approximately zero, the gas can be considered as inert nitrogen.

The results of these analyses are summarized in Table XXXVIII.

TABLE XXXVIII.

Temperature Period Analyses of Index Oil Cases

Run Number	t°	CO_2	Unsaturates	O_2	CO	H_2	CO_2 Produced	Combustion Analysis Residue	Decrease	CO_2	N_2
94-1	25-115°C.	0.56^x	11.40	2.46	0.45	6.98	0.34	---	0.00	0.00	74.86
		2.8	57.0	12.3	2.2	34.9	1.7	4.8	----	----	-----
94-2	115-145°C.	2.44	17.60	3.32	1.46	6.63	2.56	---	1.72	2.66	50.20
		6.1	44.0	8.3	3.7	16.6	6.4	39.4	----	----	----
94-3	145-177°C.	7.39	3.56	5.15	2.13	25.22	2.10	----	18.23	13.95	0.00
		37.0	17.8	26.7	10.7	126.1	10.5	271.2	---	---	---
94-4	177-225°C.	33.13	1.75	2.62	8.62	13.68	4.31	---	32.40	27.33	0.00
		82.8	4.4	6.5	21.6	34.2	10.8	89.7	---	---	---
94-5	225°C.	7.47	15.81	4.45	3.60	0.69	1.60	---	-0.06	0.69	66.38
		18.7	39.5	11.2	9.0	1.7	4.0	0.0	---	---	---
94-6	220°C.	2.94	25.80	2.13	2.34	0.33	0.60	---	-0.11	0.33	65.86
		14.7	129.0	11.6	11.7	1.7	3.0	0.0	---	---	---
94-7	220°C.	2.32	24.80	2.21	3.31	0.00	0.41	---	-0.17	0.23	66.95
		5.8	62.0	5.5	8.3	0.0	1.1	0.0	---	---	---

x - Upper figures are percentages; lower figures are cc. volumes.

The upper figures in Table XXXVIII. are determined compositions, and the lower figures are calculated volumes on the basis of the above assumptions. These lower figures have much more significance than the experimental percentages which give a false impression of the variation of each component.

The volume variations of each of the constituent gases with respect to the temperature, are plotted in Figure 50. These curves indicate the following facts:

(a) Carbon dioxide is produced in largest amounts between 150° and 200° C. Below and above these temperatures only small quantities of CO_2 have been detected.

(b) Unsaturated substances are produced in large quantities at temperatures below 150° C. and at temperatures well above 200° C.

(c) The oxygen content of the gas is erratic. Probably, the first volumes represent mechanically absorbed oxygen, and the large volumes produced around 150° C. may represent peroxide decomposition.

(d) Carbon monoxide is produced in increasing amounts up to 200° C.

(e) Hydrogen is produced in large quantities at temperatures below 200° C., but is practically non-existent above that temperature.

(f) Highly combustible unabsorbed constituents are produced at temperatures between 130° and 200° C.

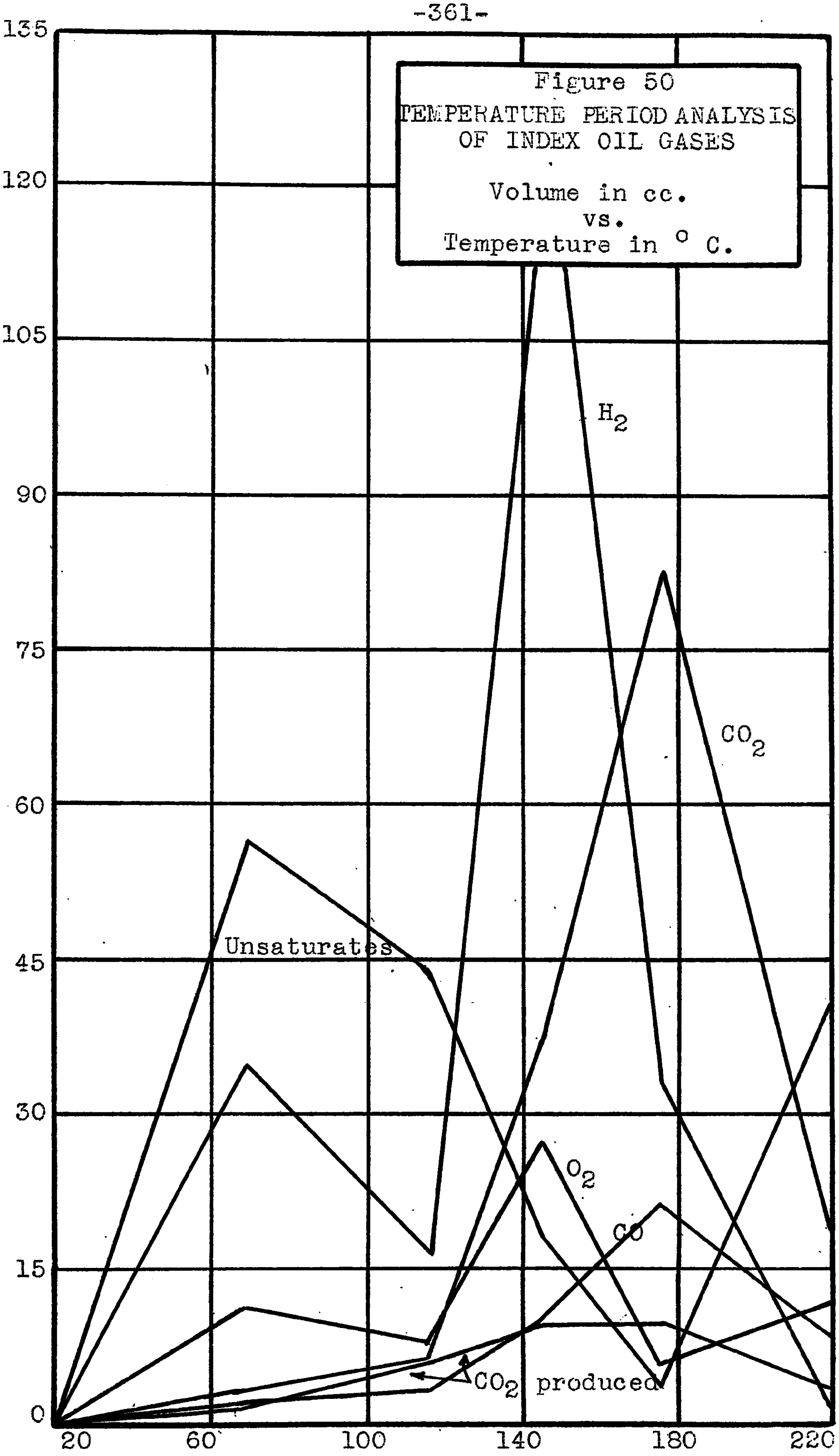


Figure 50
TEMPERATURE PERIOD ANALYSIS
OF INDEX OIL GASES
Volume in cc.
vs.
Temperature in ° C.
H_2
CO_2
Unsaturates
O_2
CO
CO_2 produced
135
120
105
90
75
60
45
30
15
0
20
60
100
140
180
220

SUMMARY

Percolator blown index oils have been produced from linseed oils, soybean oil, perilla oil, and menhaden oil.

The individual and composite effects of oil temperature, air humidity, and metallic catalysts have been studied as agents for accelerating the blowing process.

The changes in refractive index, iodine value, acid value, viscosity, specific gravity, and molecular weight have been studied over this blowing period.

Similar oxidized oils have been produced by a new pressure oxidation method which provides rapid and controlled oxidation of the oil.

The individual and composite effects of temperature, pressure, agitation and catalysts were studied in order to find the optimum operating conditions, and to gain some insight into the mechanism of the reaction.

The oxidation process has been developed for the use of air pressure on large batches of oil.

Various properties of these index oils were studied in some detail. These include drying time, resin solubility, water permeability, drier precipitation, ferric chloride gelation, and heat bodying.

THEORETICAL DISCUSSION

Oxidation Of Oils

It is known that there are two distinct periods in the production of an index oil, namely, an induction period and a period in which the various properties of the oil are changing very rapidly. Later this rapid change in properties ceases and there is a slow absorption of oxygen until the oil gels. Since index oils of minimum viscosity are desired, the oxidation process is never carried beyond the rapid change period.

The presence of an induction or incubation period has led to three major premises and has eliminated a fourth. Obviously the oxidation cannot be a straightforward process in which oxygen is added in the same manner up to a saturation point; such a mechanism would require a straight line of diminishing slope for the absorption curve. The three premises which have gained recognition are:

(a) The natural antioxidants in the oil are being destroyed.

(b) The reaction is autocatalytic; oil peroxides are being formed during this period as the reaction velocity builds up to its maximum.

(c) The oil is undergoing molecular rearrangement, involving a conjugated system of double bonds.

Evidence for all of these theories has been presented in detail in the introduction of this dissertation. Much of this evidence is conflicting and valid arguments can be proposed in favor of any one of these three theories.

The effects of natural oil anti-oxidants are well known (cf. Catalysis). Extracts from the unsaponifiable residue of the oil have been shown to increase the induction period in a manner similar to artificially added anti-oxygens, such as the phenols. On the other hand, the induction periods of Superb, SH'd and raw non-break linseed oils do not differ greatly despite the wide differences in their refining processes.

The shape of the oxygen absorption curve suggests the autocatalytic nature of the reaction. The formation of peroxides is one of the few widely accepted postulates concerning the oxidation of fatty oils. If this peroxide formation catalyzes the later oxidation reactions, autocatalysis is certainly involved. However, the catalytic effects of blown oil or benzoyl peroxide have been shown to be very small, and recent trends are away from the simple autocatalytic viewpoint. The more likely viewpoint is that antioxidants are first destroyed, after which peroxides form, rearrange, decompose and polymerize.

The idea of molecular rearrangement during this induction period seems to have a sound basis. The reactivity of the oil is considered to be increased by mechanisms which lead to a conjugated double bond system. This enhanced reactivity shows itself in the rapid changes which occur immediately after the induction period. It has been shown that, up to this point, the oil has absorbed only 1% oxygen, and that, over the rapid change period, the oxygen absorption is also only about 1%. That an oil should change so greatly with such a small oxygen intake is indicative of molecular rearrangement effects.

There are possibly three mechanisms which would lead to conjugated oil molecules:

(1) Oxidation at intermediate methylene groups to form carbonyl-type conjugated systems.

(2) Oxidation to peroxides which rearrange to hydroxyl groups and subsequently split off water.

(3) Double bond isomerism involving the random movements of protons.

The actual existence of conjugated double bonds in partially oxidized fatty oils has been shown by a number of indirect investigations:

(a) The iodine value of an oxidized oil increases with time. Since conjugated systems react 1,4 initially and then rearrange, the last double bond shows a lag in iodine absorption.

(b) The heats of combustion of conjugated systems are usually lower than those of the non-conjugated isomers. The heat of combustion has been shown to decrease during the oxidation of an oil.

(c) Conjugated double bonds react with maleic anhydride; oxidized oils also show a diene value. However, anhydrides, such as maleic anhydride, may react with hydroxyl groups in the oil and produce conjugated systems. A similar reaction has been developed for converting castor oil to a conjugated drying oil. Oxidized oils show no change in acetyl number after the maleic anhydride reaction, a fact which supports the idea of a true diene reaction. Furthermore, by determing the iodine numbers of index oil, maleic anhydride, and their reaction product, definite evidence of a chemical reaction was obtained.

(d) The refractive index of a conjugated system shows a large exaltation over that of its non-conjugated isomer; oxidized oils show similar exaltations.

(e) Oxidized oils show all the chemical properties of tung oil, a conjugated type drying oil. Of especial importance, from a conjugation viewpoint, are the similarities in heat bodying time, resin solubility, water permeability and ferric chloride gelation.

The exact mechanism which produces this conjugation is still vague; possibly, all three mechanisms are involved.

The carbonyl-type conjugation is least promising because this type molecule has not been shown to react with maleic anhydride and has no real similarity to the tung oil structure.

The formation of conjugated systems through the elimination of water is hardly feasible at the temperatures of air drying, blowing or even pressure oxidation. There is a greater probability that reactions of this sort may be taking place when oxidized oils are heated (cf. Heat Bodying). There are evidences of increased conjugation in heat-bodied index oils; these oils show an additional increase in refractive index and a greater water resistance when used in long oil varnishes.

The prototropic isomerization of double bonds seems to be the most likely conjugation mechanism. This reaction is an equilibrium in which a single proton shifts its position in either direction along the chain, but generally towards the carboxyl grouping of the acid residue. These random movements lead to conjugated systems when two or more ethanoid linkages are present in the same acid residue. In terms of the number of conjugated systems at any one time, this reaction has an unfavorable equilibrium. When a double bond is created at the α-β position, the equilibrium ceases but the molecule may be split under severe treatment.

This type of isomerism is known to be catalyzed by acids and bases. In this connection, it is interesting that definite catalytic effects were shown by both acetic acid and potassium hydroxide in the pressure oxidation of oils. Uncatalyzed oxidations did not yield index oils unless the oxygen and oil were intimately mixed; equilibrium reactions inhibited by pressure were shown not to be involved. On the other hand, index oils were produced when either acetic acid or potassium hydroxide were added. Also, the catalytic action of metallic driers was increased by the same reagents. This latter effect is probably due to the nature of the oil reactions, as follows:

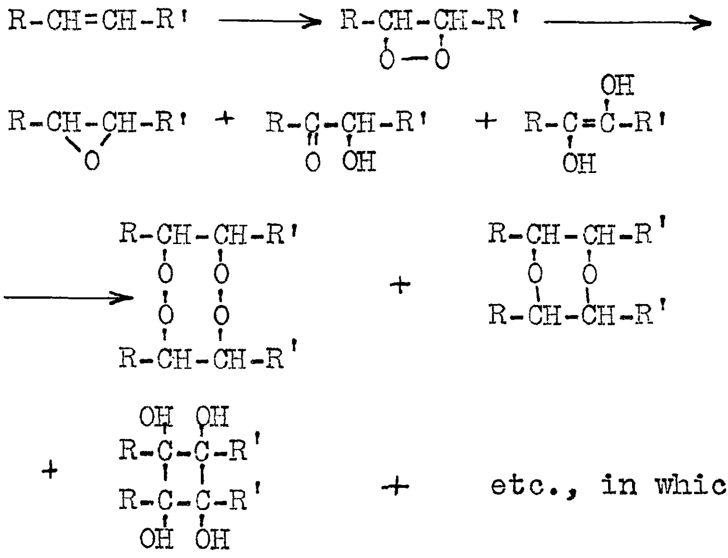
$A \rightleftharpoons B$ may represent the isomerization reaction occurring during the induction period; this is probably a rapid reaction, but the equilibrium is unfavorable.

$B \longleftrightarrow C$ may represent the oxidation and/or polymerization of these conjugated systems; this is probably a relatively slow reaction, which is strongly catalyzed by metallic driers. Thus, the metallic catalysts speed up the removal of the conjugated oil molecules and indirectly aid the equilibrium of the isomerization reaction. Acids and bases, by catalyzing the first reaction, provide a ready supply of conjugated molecules for the oxidation reaction; thus, their combination with metallic driers yields a slightly faster rate of oxidation than that of systems containing only the metallic catalysts.

Evidence has come from the Regional Soybean Industrial Products Laboratory in support of this prototropy theory. When linseed and soybean oils were acetylated, the diene numbers jumped from 2.5 and 3 to 12 and 20 respectively. The obvious conclusion is that conjugated systems have formed through isomerization of double bonds.

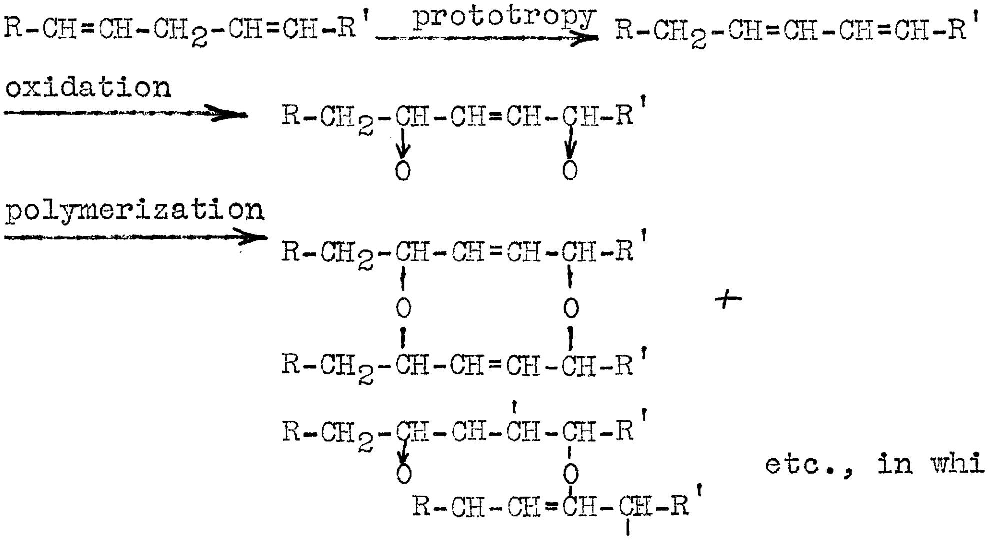
Oils can be oxidized by percolation blowing without the addition of catalysts. In this process, the isomerization catalysts might arise through a splitting of the glycerides to form acrolein and fatty acids. Acids might also be formed through oxidation at double bonds in the glyceride chains. The increase in acid number during blowing supports these ideas.

The subsequent changes during the production of index oils involve oxygen addition to form oxy, peroxy, hydroxy, and carbonyl groups, and polymerization through double bonds and/or oxygen linkages. The oxygen absorption is too small to account for the rapid changes in oil properties, and polymerization is a necessary adjunct. These mechanisms can be simply represented as peroxide formation, rearrangement, decomposition and/or polymerization as follows:



etc., in which the polymerization may be both inter and intramolecular, that is, between acid residues in the same glyceride molecule and those in two or more adjacent glyceride molecules. There are infinite possibilities in this respect, and the very complexity of the problem has prevented its final solution.

However, in line with the isomerization theory, the following mechanism is proposed:



etc., in which

the polymerization may be both inter- and intramolecular, that is, between acid residues in the same glyceride molecule and those in two or more adjacent glyceride molecules. Here, dative bonds are involved in the 1,4 oxygen addition, and as in the previous case, numerous polymerization mechanisms are possible.

Heat Bodying Of Index Oils

When index oils are heated, profound and complex changes occur, as evidenced by the data previously presented on this phenomenon.

The oil properties show unusual changes during the critical period of heating, 20°-200°C. The molecular weight shows a minimum at 150°C.; the refractive index shows a minimum at 160°C.; the acid value shows an abnormally high maximum at 150°C.; the iodine value shows a distinct minimum at 200°C.. When we correlate these facts with the indications shown by gas analysis of the volatile products, a number of interesting suggestions arise. The gases evolved during this critical period include H_2O, O_2, CO, CO_2, unsaturates, aldehydes, acids, and other highly combustible constituents. The hydrogen is produced below 200°C.; the CO_2 is largely produced between 150°-200°C.; the unsaturates are produced below 150°C. and the CO is produced in increasing amounts up to 200°C.

Several possible mechanisms are involved. Hydroxyl groups may lose water to form conjugated systems, which immediately polymerize. Such a reaction would decrease the refractive index and the iodine value, and increase the molecular weight; possibly this reaction is occurring around 200°C.

Another possible reaction would involve the decomposition of glycerides to fatty acids and olefins. These fatty acids could decompose around 170°C. to CO_2 and hydrocarbons. The olefins may later hydrolize to compounds such as acrolein or they may polymerize. These reactions would initially cause a decrease in molecular weight and refractive index, and a large increase in acid value. At 170°C. and above, the subsequent reactions would cause a rapid fall in acid value and an increase in molecular weight due to polymerization of the unsaturated residues.

Other decomposition reactions are also probably occurring at the oxidized positions. The well-known presence of acrolein suggests two other reactions:

(a) The peroxide decomposition of oxidized conjugated oil molecules (cf. Salway - Volatile Products).

(b) The oxidation of glyceryl residues.

The bodying of an oxidized oil seems to be analagous to a violent oxidation at selective points in an organic molecule. These reactions will lead to acids, aldehydes, ketones, hydroxy acids, etc. Certain of these substances are unstable to heat and can decompose further as in the following examples:

$$HCOOH \xrightarrow{160^{\circ}C.} H_2 + CO_2$$

$$HCOOH \xrightarrow{dehydrate} H_2O + CO$$

$$CH_3CHOHCOOH \xrightarrow{130^{\circ}C} HCOOH + CH_3CHO$$

$$CH_2OHCH_2COOH \xrightarrow{heat} CH_2{=}CH\text{-}COOH + H_2O$$

$$COOH\text{-}COOH \xrightarrow{heat} CO_2 + HCOOH$$

Further possibilities in this connection are discussed in the section on volatile products.

In addition to these decomposition and oxidation reactions, there are other reactions involving polymerization. Thus, an oxy-group may lose its oxygen and revert to the unsaturated linkage or directly polymerize to larger molecules; however, the most likely reaction would involve neither of these, but rather would be a rearrangement to a carbonyl group. Likewise, a peroxy-group could lose two atoms of oxygen and revert to an ethanoid linkage, or directly polymerize to larger molecules.

These and other reactions probably combine to produce the complex effects observed during the heating of an index oil.

Resin Solubility

This unique property, which is possessed by index oils and raw tung oil, seems to be somehow related to the presence of conjugated systems in the oil molecule.

In an attempt to determine whether resin 451 dissolves or disperses in index oils, the iodine values of the resin, the oil, and the heated mixture were determined. These values seem to indicate that no chemical reaction is taking place; that is, the solution effect must be of a physical nature.

Since only index oils and tung oil have this solubility property, chemical reaction should be a definite factor. The iodine value results should not be considered too highly, because of the possibilities of opposing effects, inaccuracies, and the uncertain behavior of complex resins in the presence of iodine solutions. For example, if a reaction occurred in which a conjugated three double bond system rearranged to a two double bond system with the simultaneous addition of resin molecules at the two activated positions, then the iodine value decrease would be too small to be detected.

A more likely explanation of this resin solubility would be the inhibition of cross-linking reactions. In the case of index oils, the polar groups produced during oxidation may condense with resinophore groups and give rise to a linear polymeric structure. Agents, which orient at the active points in the resin molecule, would also tend to inhibit further cross-linking. Free fatty acids are probably of this nature, and they have been shown to dissolve resin 451.

Another possible explanation is that the conjugated double bond system, being very reactive, adds to the resinophore groups and forms linear, fusible polymers.

Index Oil

The chemical and physical properties of this processed oil have been discussed in detail, its unique uses, which surpass those of raw tung oil, have been prominently exploited, but only speculations could be made concerning the chemical structure of this material.

The complex nature of the raw materials and their variable behaviors during oxidation make a definite theory impossible. The variety of reactions which apparently occur during the heat bodying of this oil, points to the complexity of this material.

These partially oxidized fatty oils (index oils) are probably complex mixtures of glycerides in various stages of oxidation, polymerization, and decomposition. Isomeric conjugated structures have been formed; peroxy- and oxy-groups are present or partially rearranged to carbonyl and hydroxyl groups; decomposition products such as acrolein, fatty acids, aldehydes, etc., are dissolved in the oil; inter- and intra-molecular polymers have been formed through carbon and/or oxygen linkages. This complex array of indefinite substances constitutes what we call "index oil".

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BIOGRAPHY

The author was born in Bethlehem, Pennsylvania on February 1, 1915 of Charles Tooke and Carrie Fried Heiberger. Several years later he moved to Allentown, Pennsylvania, where he attended grade school and high school.

He was graduated from Allentown High School in 1931 with honors and prizes in mathematics, physical sciences, political science and general scholarship.

In September, 1931, he entered Lehigh University from which he was graduated in June, 1935 with highest honors, receiving the degree of Bachelor of Science in Chemical Engineering. During his undergraduate tenure he received honors and prizes in chemistry and general scholarship, and was duly elected to Phi Eta Sigma, honorary freshman fraternity, and Pi Mu Epsilon, honorary mathematics fraternity. He was also a member of the American Chemical Society, Student Chemical Society, Newtonian Mathematical Society, and Lehigh Allentown Club.

He spent the next four years also at Lehigh University, during which time he received the degree of Master of Science in Chemical Engineering in June 1937.

From September 1935 until June 1939 he taught Freshman chemistry courses as an Assistant in Chemistry. Since July, 1939, he has been employed as a research chemist with the United States Rubber Company, Inc., in Passaic, New Jersey.

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