STUDIES ON THE HEAT POLYMERIZATION

OF

LINSEED OIL

A Thesis

by

Orville Samuel Privett

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GENERAL INTRODUCTION

A recent economic survey of edible fats and oils indicated that the world supply was only sufficient to meet slightly over one-half of the requirements for 1946. This deficit will most certainly affect Canada's overall supply in 1947, particularly as our production has declined, eg., the amount of lard produced in 1946 was only fifty percent of the 1944 production. Normally, Canada produces only about forty percent of her requirements, and since imports are controlled by the Combined Food Board, every effort is being made to increase our domestic production.

Linseed oil comprises by far the largest proportion of the vegetable oil produced in Canada and if it could be utilized for edible purposes it would assist materially in alleviating prevailing shortages of food oils. Some linseed oil is being used in the manufacture of shortening but the amount has to be strictly limited because of the undesirable flavour and odour its products acquire in baking.

The problem of "flavour reversion" in linseed shortenings has recieved considerable attention in recent years and improved products have been obtained, but the undesirable flavours and odours have never been completely eliminated. There is considerable evidence that linolenic acid is the main source of the trouble. Linolenic acid is known to be more

susceptible to the action of heat than the other component acids of linseed oil. The ensuing investigation, therefore, is primarily concerned with a study of the nature of heat polymerization with the object of establishing the conditions of thermal treatment of the oil which would eliminate "flavour reversion" in the final shortening.

The polymerized portion of the oil segregated with acetone corresponds to the most highly unsaturated fraction of the original oil and hence has special value as a drying oil. Further segregation of the polymer fraction with acetone yields a low viscosity oil and a high viscosity oil. The high viscosity oil has excellent properties as a varnish ingredient, whereas the low viscosity oil is highly desirable for other uses in the drying oil industries.

The research described in this thesis has culminated in the development of a process involving heat polymerization and solvent segregation of alkali-refined linseed oil to produce a number of oils with different properties, one of which can be used for the manufacture of shortening and the others have properties highly desirable in drying oils.

REVIEW OF THE LITERATURE

A. Heat Polymerization of Linseed Oil.

Studies on the heat polymerization of linseed oil in the production of litho oils were first reported at the turn of the century by a number of workers (18, 31, 39, 55). Of this group, Lewkowitsch (31) was the first to recognize that the thickening process in the production of these oils was polymerization. At this time, however, the chemical changes were not fully understood and Lewkowitsch used the term more for convenience than to describe specific reactions.

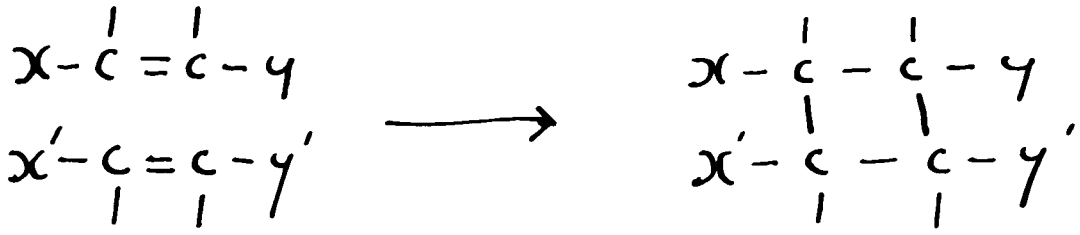
Although the thermal treatment of vegetable oils is a very old and common industrial practice, progress in the elucidation of the chemistry of polymerization has been slow. Perhaps the chief reason for this is the great diversity of industrial processes embodying thermal treatment for the production of many different types of oils. The various thermal processes now in use can be classified into two general groups, (a) those in which polymerization is effected largely through the agency of heat, and (b) polymerizations in which oxidation plays a prominent role. Most of the oils now used in the manufacture of protective coatings are heat polymerized oils and this investigation is concerned particularly with

the chemical and physical changes involved in this type of polymerization as applied to linseed oil.

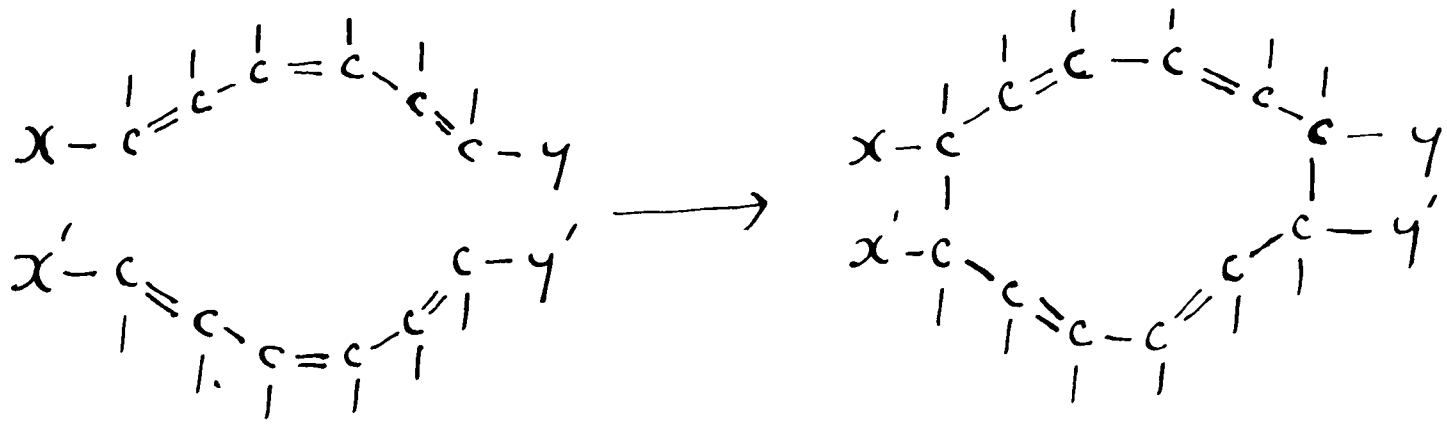
In 1920, Salway, (43), suggested that in the initial stage of polymerization one or more fatty acid radicals are liberated which condense with the unsaturated linkages of the fatty oil. Staudenger (46), believed that there are two types of polymerization, (a) "true" polymerization in which the atoms are united as in a monomolecular product, that is by primary valences, and (b) "condensing" polymerization which involves a "shifting of atoms".

The studies conducted at that time were mainly concerned with the polymerization of the intact oils, and since the triglyceride molecule is capable of forming complex linear and three-dimensional polymers, the elucidation of the reaction mechanism was extremely difficult. It is now generally agreed that only the unsaturated fatty acid chains of the glyceride molecules are involved in the polymerization, and hence most of the recent studies have been made on the monohydric alcohol esters of higher unsaturated fatty acids (2, 8, 11, 12, 28). The formation of complex polymers is thus avoided and, although little is known about the nature of the compounds in polymerized oils, considerable progress has been made in elucidating the mechanism of the reactions involved in their formation through study of the polymerization of the fatty acid esters,

Morrell (36), advanced the theory that dimers are four-membered carbon rings, the formation of which involves the double bonds according to the following equation:



Rossman (42), suggested that in the polymerization of eleostearic acid dimers containing a twelve-membered carbon ring were formed by the following reation:

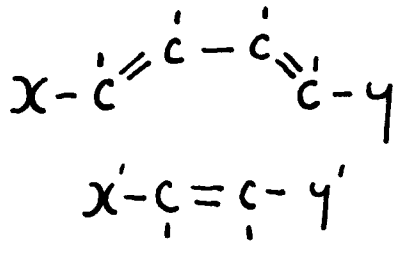


The modern conception of the mechanism of the polymerization of drying oils is based on experiments conducted by Morrell, in 1915, (35). He found that polymerization was preceded by a shift in the position of the unsaturated linkages in the molecules, and also that the polymerization involved the doubly-linked carbon atoms. These findings formed the basis of Scheiber's isomerization theory (45). Scheiber was the first to realize that the initial reaction in the thermal treatment of drying oils is the formation of conjugated isomers. This he deduced from the observation that the refractive index of linseed oil increased on heating, whereas that of tung oil decreased (44).

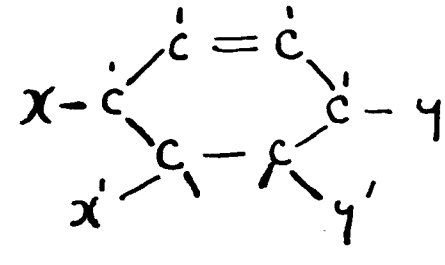
These original observations were later developed into a theory of polymerization (45) which assumes this shifting of double bonds as the initial reaction. The formation of conjugated isomers in polymerization has also been observed in linseed oil by Taylor and Smull (51), and in purified ethyl linolenate by Steger and van Loon (48). Brod, France and Evans (12) found that thermal treatment of 9, 11 and 9, 12 linoleic acid esters produced identical polymers, this indicating that the ordinary 9, 12 acid was isomerized to the 9, 11 form. Further evidence for the formation of conjugated isomers was obtained in more recent studies on the ultraviolet absorption spectra of polymerized linseed oil, (Bradley and Richardson (10), Mitchell and Kraybill (34).

To elucidate the mechanism of the reaction Kappelmeier (25) proposed dimer formation by a modified Diels-Alder reaction (16), with the formation of a hydroaromatic six-membered carbon ring. This is in accordance with Scheiber's isomerization theory as the double bonds of at least one of the molecules must be conjugated before the reaction can proceed. The reaction is presumed to take place as follows:

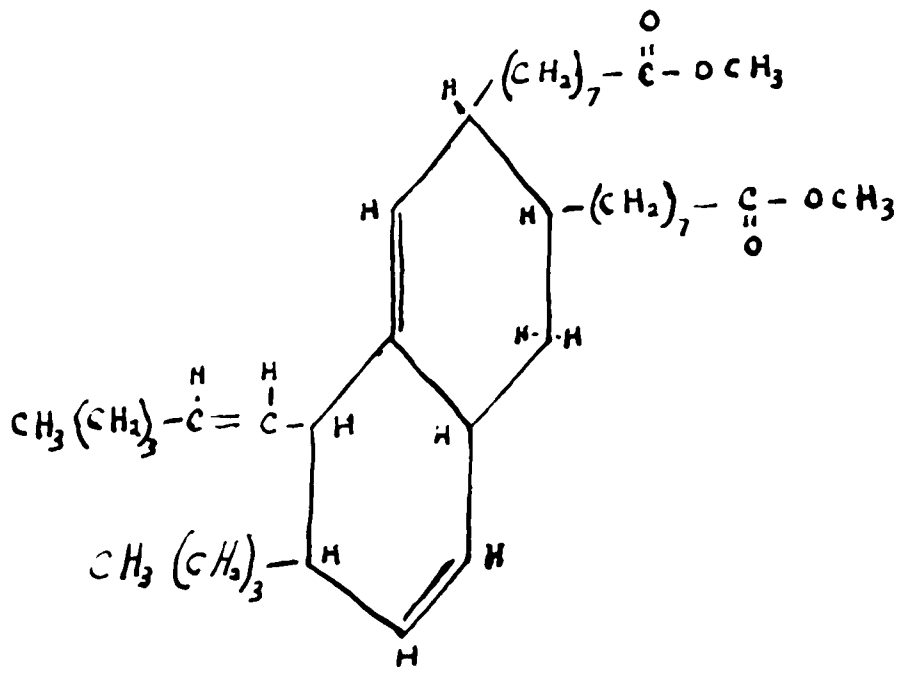
Monomer



Dimer

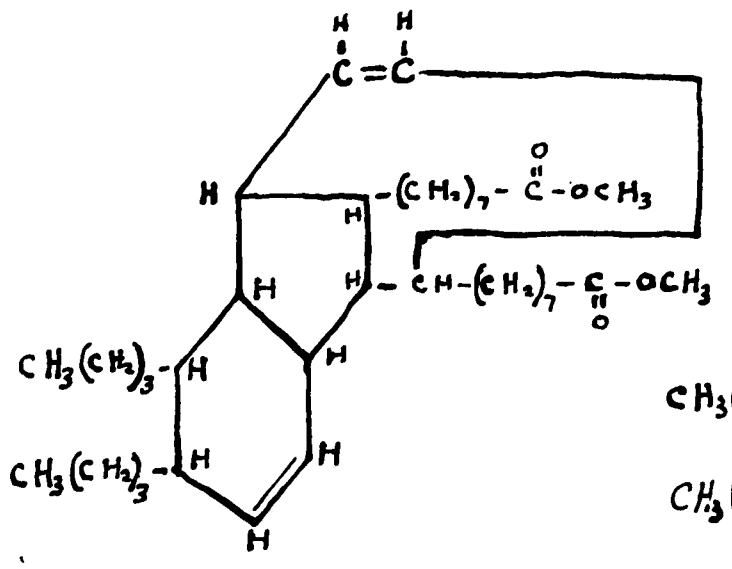


It is now conceded that the mechanism of the reaction is essentially that proposed by Scheiber, namely, isomerization as the initial reaction followed by polymer formation through a modified 1, 4 diene addition reaction as first suggested by Kappelmeier. However, although there is general agreement as to the mechanism of polymerization, there has been much speculation and lack of agreement as to the nature of the products of the reactions. Bradley and Johnston (8), believe that in the polymerization of methyl eleostearate the reactions involve the formation of a bicyclic dimer by a complex reaction which involves a shift of hydrogen and an unusual ring closure:

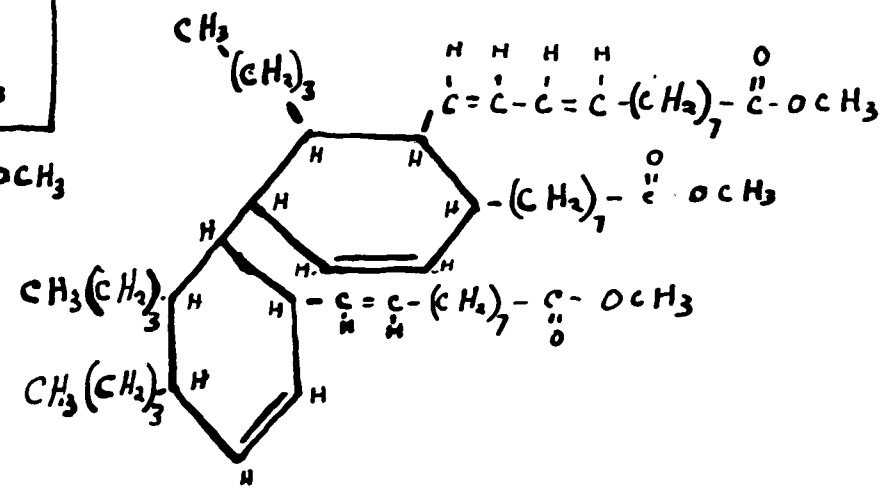


On the other hand, Ault and co-workers (2) postulate the formation of a tricyclic dimer and a bicyclic trimer by a simplified interpretation of a 1, 4 diene addition mechanism:

Tricyclic Dimer



Bicyclic Trimer



In these investigations the polymerizations were carried out under widely different conditions so it is not surprising that different products were obtained. The differences in the suggested structures, however, appear largely to be due to a difference in the degree of unsaturation as measured by iodine values. Ault and co-workers (2), find that a range of iodine values is given by the different methods depending on the duration of the reaction time. Morrell (37) also found that Wigs' reagent has a Wijs depolymerizing effect. Hence, it must be realized that physical and chemical analyses may be difficult to interpret because of inherent limitations in the usual analytical methods. Until more is known about the relationships which

exist between these complex molecules and their physical and chemical properties, it will be difficult to elucidate their exact structure.

Application of the general polymerization theory to the chemistry of the drying oils has been attempted by a number of workers (6, 7, 9, 47). Although little is known about the nature of the components of polymerized oils, the basic concepts established in the polymerization of the monohydric alcohol esters of the higher unsaturated fatty acids appear to hold for the triglyceride molecule. The reactions are not regarded as being different from those occurring between ordinary organic compounds but rather a peculiar multiplicity of these reactions.

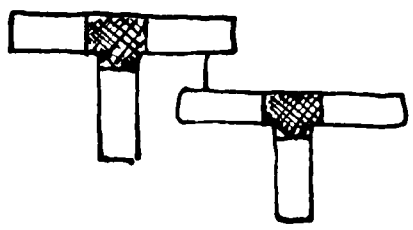
Certain aspects of polymerization have been clarified by applying the theory of polymerization developed on the concept of functionality in the molecule (13, 14, 26, 27). According to this theory those molecules containing one reactive group are called "monofunctional"; those with two reactive groups "bifunctional". For a high degree of polymerization the molecules must be at least bifunctional as with monofunctional molecules all the functional groups are used up in the formation of dimers. Bifunctional compounds are capable of continued linear polymer formation as only one functional group is involved in the linkage of two molecules, and the product still retains the same

degree of functionality. However, if the compound has three or more functional groups there will be a progressive increase in functionality as polymerization proceeds; the polymers become more reactive and three-dimensional cross bridging between adjacent chains result to form solid, rigid structures. An unsaturated fatty acid normally has one functional group, but when the triglyceride molecule contains three unsaturated fatty acids it will have three functional groups and hence can form complex three-dimensional polymers. Although all unsaturated fatty acids are one functional group, they differ in their reactivity under the influence of heat (8, 12). Linolenic acid is more readily polymerized by heat than linoleic acid which is, in turn, less stable than oleic acid, while the saturated acids are the most resistant. Since it is possible to have twenty different types of triglyceride molecules (considering all the saturated acids as a single class), some trifunctional and other bifunctional, and since reactivity to heat depends on the fatty acid composition, the elucidation of the reactions involved and the nature of the products obtained becomes exceedingly difficult. The reactions are further complicated by the fact that intramolecular cycilization (49), and decomposition reactions (8, 11) take place under various conditions. Evidence for the formation of polymers from the products of thermal decomposition is presented by Bradley and Johnston (8, 11). They believe that rupture of the

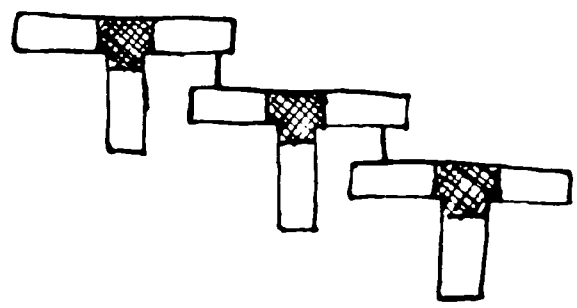
fatty acid chain yields octenes and octadiens which undergo polymerization to give low molecular weight polymers. The polymerization of the drying oils is evidently a very complex process.

In discussing the analyses of a very thoroughly heat-gelled drying oil, Bradley and Pfann (9), use the following configurations:

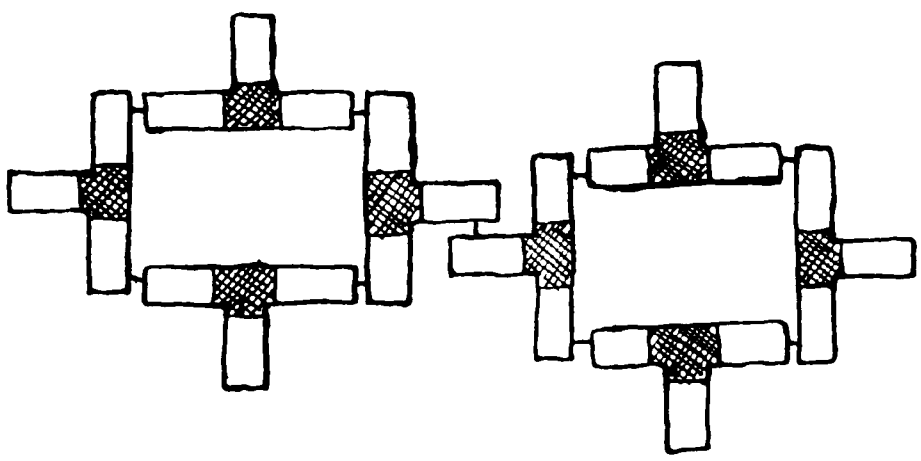
DIMER



TRIMER



The small black "T" represents the glyceride radical which is attached through ester linkages to three linear fatty acid radicals indicated by the clear blocks. They believe that the predominate structure in a thoroughly heat-gelled drying oil is a molecular aggregation consisting of eight triglyceride molecules, arranged as illustrated below. This concept represents the extent of our progress in elucidating the constitution of polymerized oils:



Heretofore little or no emphasis has been placed on the affect of the conditions of polymerization on the nature of the resulting products. The investigations recorded in this thesis reveal that the temperature of polymerization not only influences the rate of the reaction, but also affects the nature of the products obtained. At the lower temperatures polymerization is selective and the reactions proceed in a definite and uniform sequence. The effect of temperature on polymerization was first observed in 1915, by Morrell (35), who suggested that polymerization takes place in two stages; one below 280°C, and the other at higher temperatures. However, this selectivity of the reaction at the lower temperatures is to be expected because the rate of the reaction is much slower, and hence the various molecules should have different rates of reactivity towards the action of heat. Since,under these conditions of polymerization, the reactions proceed in a uniform sequence and side reactions are reduced to a minimum, the analytical data affords a clearer and more detailed interpretation of the primary polymerization reactions. A study of the nature of these reactions, under these conditions, was initiated. The results, detailed below, suggest that the polymerization proceeds selectively according to the level of unsaturation in the triglyceride molecule.

B. FLAVOUR REVERSION IN LINSEED SHORTENINGS

Although the hydrogenation of linseed oil takes considerably more hydrogen than edible oils normally require, the greatest obstacle to its utilization in the manufacture of shortening is that it is subject to a type of deterioration termed "flavour reversion". The term "reversion" has commonly been used to describe a group of "off" flavours and odours which develop on heating or storing linseed and soybean products. It has been pointed out by Armstrong and McFarlane (1) that "reversion" does not imply the return of flavours and odours previously present, but refers rather to the development of new flavours and odours which are unique and characteristic. This is particularly true of linseed shortening. The undesirable flavours develop either on storage or when the products are subjected to baking or frying temperatures. In the past decade many workers have studied the causes of reversion in linseed and soybean oils and their hydrogenated products (4, 17, 20), and a number of sources of the undesirable flavours and odours have been suggested, such as:

(a) The highly unsaturated fatty acid, linolenic acid (1, 3, 40, 30).

(b) Oxidation products of the natural antioxidants (29 p, 131, 4).

(c) Nitrogen containing substances (52, 15).

Recent work by Lemon (30), and by Armstrong and McFarlane (1), strongly indicates that linolenic acid is responsible for the reversion of linseed shortenings through its conversion to an isolinoleic acid in the hydrogenation process. This acid was shown by Lemon to undergo oxidation to yield products which have the typical reverted odour and flavour. The prevention of reversion has been attempted by modifying the customary steps in processing the oil (1, 30), and by special treatments, including the use of antioxidants. However, although improved products have been obtained, flavour reversion has never been completely eliminated.

The investigations recorded in this thesis include a study of the conditions of thermal treatment of linseed oil which bring about the isomerization or polymerization of the linolenic acid, and thereby eliminate flavour reversion. Shortening prepared from the heated oil does not revert. However, since the high polymer fraction is less nutritious, and may even be injurious to health, the polymerized oil is fractionated with acetone. The acetone-soluble fraction makes a most acceptable shortening. The yield of acetone-soluble oil and the quality of the shortening obtained depends on the

conditions of polymerization. The heat polymerization, solvent segregation, and hydrogenation of alkali-refined linseed oil have been studied to establish the optimum conditions for the production of a shortening of the best quality.

METHODS

1. Heat Polymerization.

The heating medium is a salt mixture composed of 55 parts potassium nitrate and 45 parts sodium nitrate which melts at 227°C. It is contained in an enamel saucepan (A) (Figure 1), which is set in a shallow sand bath on a 1000 watt insulated hotplate (B). The molten salt is stirred with an electric stirrer (C), and the temperature is controlled to within ±0.5°C by a mercury-immersion, contact thermostat (D) connected to a 250 watt immersion heater (E). About 275 grams of oil are weighed into a 500 ml. Erlenmeyer flask fitted with glass tubing connections to permit the passage of carbon dioxide through the sample at a rate sufficient to agitate the oil. When the bath is at the required temperature, the flask is immersed in the bath so that when the oil has reached the bath temperature the surface will be approximately at the same level as the surface of the heating medium. This precaution is necessary to avoid the charring of volatile products on the surface of the flask which occurs when the flask is too deeply immersed. It requires 30 minutes for the oil to reach the bath temperature. Samples, amounting to a few drops of the oil, are taken at 45-minute intervals and cooled rapidly to avoid oxidation.

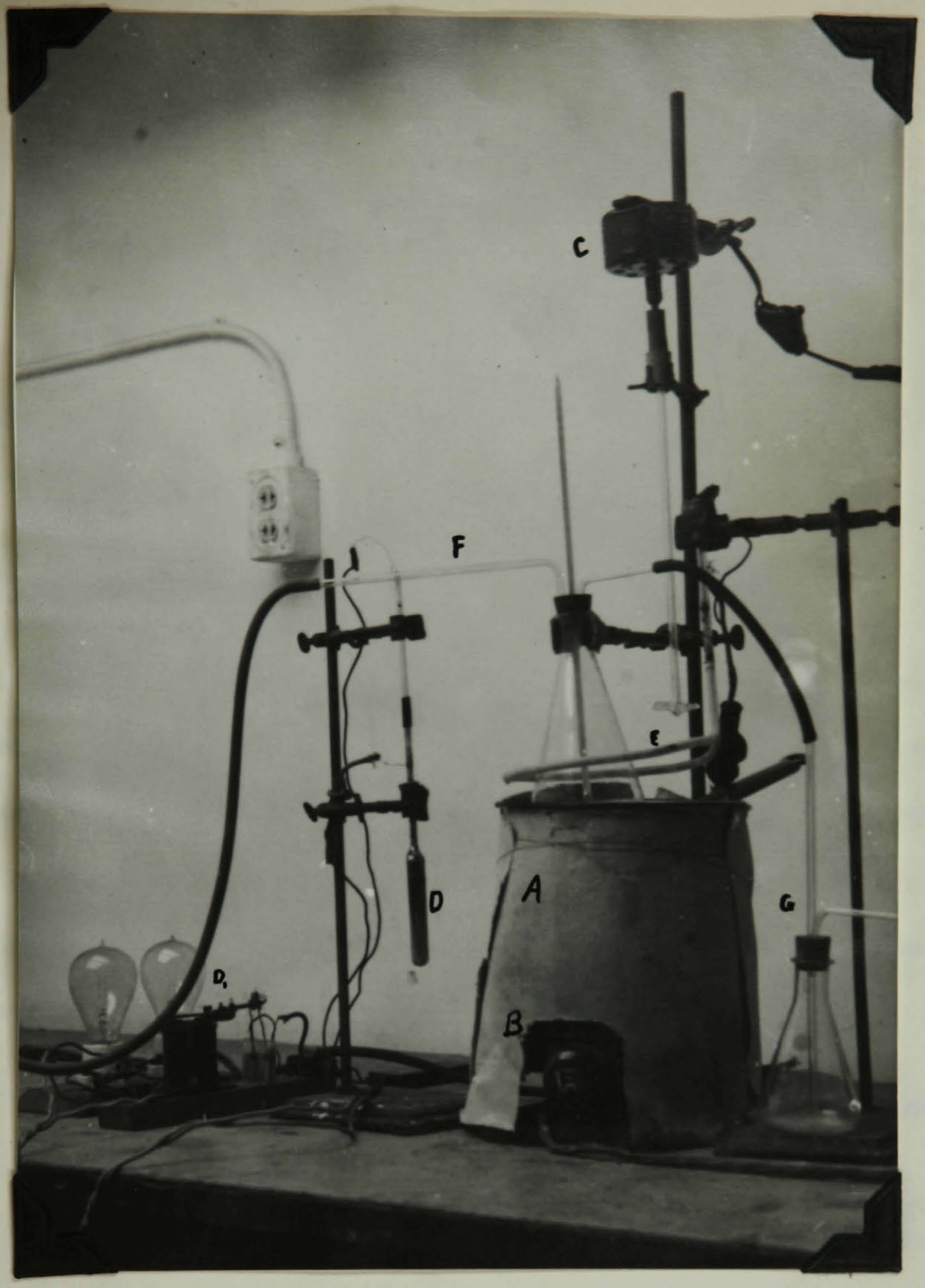


Figure 1 - Polymerization Apparatus.

A. Enamel container (8" wide x 5" deep).
B. 1000 watt insulated hotplate.
C. Electric stirrer.
D. Mercury-immersion contact thermostat.
D. Relay and resistance.
E. 250 watt immersion heater.
F. Carbon dioxide inlet.
G. Carbon dioxide outlet and trap.

The refractive index of each sample is determined at 25°C using an Abbe refractometer with the prism temperature regulated by water from a Hoppler Ultra-Thermostat. At the end of the heating period the flask is raised from the bath and the passage of carbon dioxide is continued until the oil has cooled to room temperature.

2. Solvent Segregation.

A suitable solvent for the segregation of polymerized oils must be immiscible with the oil at the temperature employed, and must selectively dissolve the non-polymeric fraction of the oil. Acetone which possesses these properties can segregate polymerized linseed oil into three distinct fractions:

(i) a non-polymeric oil which is considered non-polymeric in nature as it contains no dibasic acids,

(ii) a low polymer fraction which is slightly soluble and is extracted very slowly, and

(iii) a highly polymerized fraction which is insoluble.

By adjusting the conditions of extraction or segregation including time, temperature and ratio of solvent to solute, a number of oils, of "bodies", or viscosities intermediate between the low polymer and highly polymerized fractions can be obtained.

A small portion of the polymerized oil (3 to 4%) is

soluble in 95% methanol. This fraction is dark in colour, has a rather obnoxious odour and strong reducing properties. It has a low refraction index (1.4778 at 25°C) and a low acid value and is believed to consist of the non-volatile decomposition products.

(a) Batch extraction.

After experimenting with various methods of fractionation, the following procedure was adopted:

The polymerized oil is poured into 1500-1700 ml. (six-seven volumes) of acetone in a round-bottom flask. The solution is mixed by gentle shaking as it is brought to boiling temperature on a steam bath, allowed to cool and let stand overnight at room temperatures. The supernatant is decanted from the insoluble oil; the acetone is distilled off and the last traces removed under reduced pressure. The amount of oil which dissolves in acetone depends on the ratio of solvent to oil and on the temperature, other factors being constant. When the polymerization is carried out for 12-15 hours at 270-275°C and the ratio of solvent to oil is 7:1, up to 60% of the oil is soluble at room temperature. An acceptable shortening can be produced from this acetone-soluble fraction, however, a sharper separation of the polymerized and non-polymer fractions is obtained if the segregation is carried out at 5°C.

(b) Liquid-liquid extraction.

Acetone is employed as the solvent and the extractions are carried out in the apparatus shown in Figure 2.

Thirty grams of oil are weighed into the extractor, approximately an equal volume of acetone is added and the mixture is shaken until all the acetone is taken up by the oil. The oil is saturated with acetone to ensure uniformity and a high degree of selectivity in extraction. If the oil is not saturated with acetone prior to extraction, the oil separates into two layers and the process is not so selective. The temperature is controlled by immersing the extractor in a water bath usually maintained at 20°C. The extraction time is about 24 hours, depending on the degree of polymerization, and on the size of the sample. The course of the extraction is followed by taking extract cuts at various intervals and determining the yield and refractive index of the oil.

3. Ultraviolet Absorption Spectra.

Conjugated double-bbnd systems absorb strongly in the ultraviolet region of the spectrum, diene conjugation exhibiting a strong maximum at 2320-2340Å, and triene conjugation at 2700Å. Since, in the thermal treatment of linseed oil the initial reaction involves the formation of

Figure 2 - Liquid-liquid Extractor.

A. Heating unit.

B. Extraction unit.

C. Funnel.

D. Condenser.

conjugated isomers, studies were made on oils polymerized to various stages and also on various segregates of these oils. A Beckman quartz photoelectric spectrophotometer was used to obtain the absorption data.

A weighed amount of oil is dissolved in purified diethyl ether and dilutions are made when necessary to give optical densities between 0.2 and 0.8. The length of the pptical cell is one cm., and the data are expressed in terms of the specific absorption coefficient according to the following formula:

$$\text{Specific } \alpha = \frac{\log_{10} \frac{Io}{I}}{cl}$$

α = absorption coefficient.

Io = intensity of radiation transmitted by the solvent.

I = intensity of radiation transmitted by the solution.

c = concentration of solute in grams per 1000 ml.

l = length in centimeters of solution through which the light passes.

4. Chromatographic Analysis.

Chromatographic analysis was carried out on the oils readily soluble in acetone which are non-polymeric in nature, the object being to determine the extent of unsaturation of the

component glycerides at various stages of polymerization. Walker and Mills (54), found that through adsorption on activated aluminium oxide, the various levels of unsaturation of the component glycerides of linseed oil could be determined. The most highly unsaturated glycerides were adsorbed at the top of the column while those of less unsaturation were adsorbed to a less degree according to the level of unsaturation.

In the segregation of the component glycerides of linseed oil the author employs the size of column used by Walker and Mills. Aluminium oxide, activated by heating at 250°-300°C for three hours is used as the adsorbent. The column is prepared by pouring a thick cream of the freshly activated aluminium oxide in benzin into the glass tube. The column is then tapped gently on the side until the adsorbent has settled and the rate of filtration (150-200 ml. per hour) is adjusted by means of suction.

It was found necessary to modify the technique employed by Walker and Mills in order to segregate the component glycerides of the acetone-soluble oils. These oils consist of triglycerides with a much narrower range of unsaturation, and thus it is difficult to obtain a complete development of the chromatogram. The following procedure was finally adopted:

Fifty ml. of an approximately 6% solution of the oil in Benzin is added to the column. The more highly saturated glycerides are eluted by continued washing with Benzin. Elution is discontinued after about twelve hours although a very small quantity of oil is still being eluted from the column. The remaining glycerides are then completely eluted with about 300-400 ml. of diethyl ether. The original oil is thereby segregated into a more highly adsorbed fraction and a fraction which is eluted with Benzin. Although this method does not give a complete segregation of all the glycerides, the most highly unsaturated are adsorbed and thus separated from the more saturated.

5. Fractionation of the Fatty Acids.

The presence of dibasic and isomerized acids in polymerized oils precludes the usual method of fractionation by the lead salt-ether process (33). However, the fractionation can be accomplished by a modification of the Twitchell lead salt-alcohol procedure for the determination of the solid fatty acids (52). It was found that the lead salts of the dibasic acids are insoluble in 95% ethyl alcohol. The alcohol-insoluble lead salts of the fatty acids of the most highly polymerized acetone insoluble segregates of oils polymerized to various stages, yield

fatty acids which have molecular weight of 560-570 indicating that these are dibasic fatty acids. However, this same fraction of the fatty acids of the whole polymerized oil yields an alcohol-insoluble fraction of fatty acids with a molecular weight only slightly over 400. This indicates that the dibasic acids are contaminated with monobasic acids. It is well-known that certain isomers of oleic acid, for example, are insoluble in 95% ethyl alcohol, and since isomerization is one of the most important reactions in polymerization, some monobasic acids are formed which are highly insoluble in 95% ethyl alcohol. The absence of these acids in the most highly polymerized fraction of the oil suggests the presence only of that portion of these isomers which have undergone polymer formation or intramolecular reaction, or that only the fatty acids of higher unsaturation are involved in the formation of the highly polymerized fraction.

Baughman and Jameison (5) showed that the lead salts of the solid acids can be dissolved in 95% ethanol at boiling temperatures and precipitated at low temperatures, while the unsaturated fatty acids remain in solution. Hence it is possible to fractionate the fatty acids into the solid, unsaturated and dibasic acids taking into consideration the limitations previously mentioned.

Ordinarily the solid acids of linseed oil consist of only saturated acids, however, solid isomers of some of the unsaturated acids are formed by the heat treatment as indicated by the iodine absorption values of these fractions. The procedure for the fractionation is as follows:

Approximately 6 grams of polymerized oil are weighed into a 250 ml. Erlenmeyer flask and the saponification is carried out with 50 ml. of alcoholic potash (40 gms. KOH per litre) in the usual manner (24). After saponification, a few drops of phenolphthalein indicator (1% alcoholic solution) are added and the excess alkali neutralized with glacial acetic acid. Ten grams of lead acetate are dissolved in 100 ml. of 95% ethyl alcohol. Both solutions are heated to boiling on a steam bath and the lead acetate solution is poured into the alcoholic soap solution. If it is necessary to acidify the 95% ethyl alcohol solution with glacial acetic acid to dissolve the lead acetate, the final soap solution must be adjusted back to almost neutrality with alcoholic potassium hydroxide. This is indicated by the voluminous white precipitate of basic lead acetate. This solution is maintained at boiling temperature for about 5 minutes on a steam bath, 0.5 ml. of glacial acetic acid is added and the solution is refluxed, generally for 15-20 minutes, until all the precipitated basic lead

acetate is dissolved. The lead soaps of the dibasic acids adhere to the sides and bottom of the flask, and the alcoholic solution of the lead salts of the unsaturated and saturated acids is decanted into a 250 ml. centrifuge bottle. The lead salts of the dibasic acids are washed twice with 10 cc. portions of 95% ethyl alcohol, and the washings are added to the centrifuge bottle which is placed in a refrigerator at -5°C. for at least five hours. The solution is then centrifuged and the alcoholic solution of the lead salts of the unsaturated acids is separated by decantation. Approximately 100 ml. of diethyl ether are added to the lead salts of the saturated acids in the centrifuge bottle, the mass is broken up by warming and shaking and the centrifuge bottle is placed overnight in the refrigerator at 5°C. The suspension is then centrifuged and the supernatant decanted. The diethyl ether solution is added back to the unsaturated fraction when it is decomposed as follows:

The alcohol is removed from the lead salts of the unsaturated acids by distillation, preferably under an atmosphere of carbon dioxide, leaving a thick, viscous liquid. The three fractions, that is the lead salts of the saturated-unsaturated and dibasic acids, are decomposed with hydrochloric acid, extracted into diethyl ether, washed, dried, and weighed in the usual manner (32).

6. Iodine Absorption.

The Rosenmund-Kuhnhenn (41) and the Kaufmann (23) methods were studied. The Kaufmann method was chosen because with polymerized oils the end point of the titration is more sharply defined. In the Kaufmann method absolute methanol is used in place of glacial acetic acid in the preparation of the reagent; this is also much more convenient to use than the highly corrosive glacial acetic acid reagent. The results by this method agree closely with those obtained by the Hanus procedure (33) when a reaction time of two hours is used. As with most methods, the results by the Kaufmann method also vary with temperature and sample weight (48), so these must be maintained, comparable in repeated analyses.

7. Hydrogenation and Deodorization.

The shaker-type of apparatus (Figure 3), the catalyst (reduced nickel on silica-gel base) and the general conditions of hydrogenation and steam deodorization are the same as was employed by Armstrong and McFarlane (1). However, to facilitate the taking of samples during the course of hydrogenation, the reaction chamber is fitted with 4 mm. copper tubing inserted through the stopper and with a valve on the outlet. The course of hydrogenation is followed by noting the hydrogen consumption and by measuring the refractive indices ($60^{\circ}C$) of the samples of the filtered oil.

Figure 3 - Hydrogenation Apparatus.

A. Hydrogen storage tank.
B. Reaction chamber.
C. Valve outlet.
D. Hyvac pump.

The catalyst contains 28% nickel. With 4% of the catalyst and a temperature of 170°C the hydrogenation time is generally about 45 minutes. The catalyst is removed by suction filtration on paper in a Buchner funnel.

An all-glass apparatus (Figure 4) is employed for steam deodorization at 180°C and 5 mm. pressure. The process is completed within three hours. Occasionally it is necessary to refilter the oil after deodorization to remove the last traces of catalyst.

8. Quality of Shortening.

Since no chemical method has yet been devised for the detection of flavour reversion, the quality of each sample of linseed shortening is assessed by baking pie crust and comparing its flavour and general quality with pie crust prepared with commercial shortenings. The grading is done by a panel, usually comprised of ten experianced judges.

9. Toxicity Test.

The toxicity test was carried out with rats. In the first test fifteen nine-week old rats were divided into three groups. The basal diet contained 15% protein and was composed of finely ground barley plus a protein and a mineral supplement. The diet of the first group was supplemented with 10% linseed oil; the second group with 10% acetone-soluble oil, and the third group with 10% alcohol-acetone segregated oil. The rats

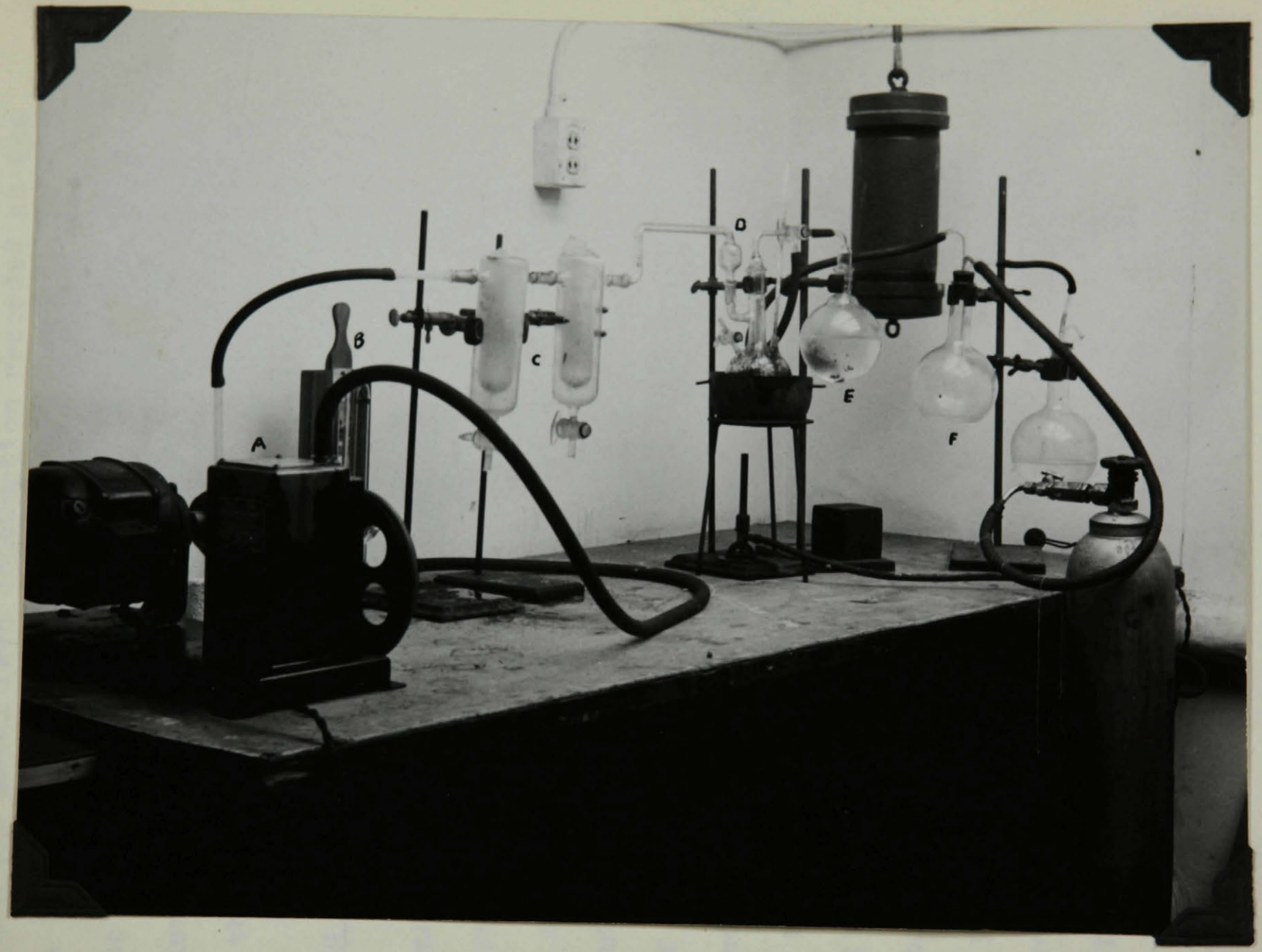


Figure 4 - Deodorization Apparatus.

A. Hyvac pump.
B. Manometer.
C. Condensers.
D. Reaction flask.
E. Source of water vapour.
F_1 and F_2 - Flasks serving to regulate the release of the vacuum.
G. Carbon dioxide cylinder

were housed in individual wire cages with food and water provided ad libitum. The rats were weighed at frequent intervals and the total feed consumption recorded at the end of the tests. The duration of the tests varied from ten days to one month. The second test was carried out in a similar manner to the first but with five week-old rats, and three extra rats were fed the basal diet only.

10. Enzymic Hydrolysis.

The pancreatic lipase solution is prepared from fresh pig's pancreas in the usual manner (50). The oils to be tested are emulsified by adding O.I.N. sodium hydroxide until the mixture is slightly alkaline to phenolphthalein. Five ml. of the oil emulsion and 5 ml. of lipase solution are pipetted into a 125 ml. Erlenmeyer flask, shaken and placed in an oven at 37°C. A blank is prepared at the same time by neutralizing 5 ml. of lipase solution with O.I.N. alkali until it shows a faint pink colour to phenolphthalein. As hydrolysis proceeds the flasks are removed from the incubator at frequent intervals and titrated with O.I.N. alkali to a faint pink colour, comparable to the blank.

11. Molecular Weight Determination.

The molecular weights of fats and oils are generally determined by the cryoscopic method, the essential requirements

being that no association takes place between solvent and solute (37,38) and that the solvent is easily crystallizable. Camphor has proven to be an excellent solvent. Its very high molecular melting point depression constant has reduced the technique merely to taking the melting point in the conventional manner. The determination is carried out by a modification of the Rast camphor method using sealed capillaries (38).

12. Viscosity.

The viscosities of the paint oils were determined with a Gardner-Holdt Bubble Viscosimeter having a range of 0.5 - 148 poises.

The sample tube is filled with oil until the air bubble is the same size as that in the standard tubes. The tubes are placed in a water bath at 25°C to bring them all to the same temperature. They are then held in an upright position with the sealed ends at the bottom and quickly inverted. The sample tube is then compared with the standard tubes to find the one which gives the same bubble test. The bodies of the paint oils are expressed in Gardner-Holdt units.

13. Colour.

The measurement of colour is made with a Helliger comparator using the Gardner colour standards of 1933. The colour is expressed in Gardner units.

14. Tolerance of Mineral Spirits.

Approximately 10 grams of oil are weighed into a 500 ml. Erlenmeyer flask and mineral spirits is run in from a burette until the solution becomes turbid. The end point of the titration is sharply defined. The value is calculated according to the following equation:

$$\frac{\text{Ml. of mineral spirits}}{\text{weight of sample}} \times 100$$

The tolerance is very high when the value exceeds 3500, 2800-3500 indicates "high tolerance" while the minimum requirement is about 1500.

15. Drying Time.

Drying tests are made by pouring the varnish or oil on a glass plate and allowing to drain in a vertical position so as to get a film approximately six inches long. At periodic intervals the film is touched lightly with the finger at a point about two inches from the top to determine the time required to change from a wet to a tacky condition, referred to as the "initial set". The varnish or oil is considered "dried hard" when no distinct impression is made when pressed firmly with the finger tip.

16. Varnish Vehicle.

Varnishes were prepared according to the following formula:

200 lb. modified phenolic resin
45 gallons polymerized oil
5 gallons fire-bodied linseed oil
85 gallons mineral spirits.

The modified phenolic resin and half of the polymerized oil is heated to 560°F., the remainder of the polymerized oil is added and the solution held at the same temperature until a drop of the material on a tin plate cools to a clear, homogeneous mass which the varnish maker refers to as "clear pill". The linseed oil is added, the product cooled and reduced with mineral spirits.

EXPERIMENTAL

I - POLYMERIZATION STUDIES

A. General.

Small samples of 250-275 grams of commercial, alkali-refined linseed oil were subjected to the heat polymerization process at various temperatures from 260-300°C for periods up to 27 hours. The results presented in Figure 5 show that, in the initial stages, a linear relationship exists between the refractive index and the time of heating, whereas in the latter stages, the refractive index changes in relation to time of heating appear as a series of uniform steps. This is especially apparent at the lower temperatures when the reaction rate is slower. The iodine absorption values change in a similar manner but inversely to the refractive indices (Figure 6). This inverse relationship is not unexpected in view of Scheiber's isomerization theory which postulates a shift of double bonds to conjugate positions. In general, conjugated isomers have higher refractive indices and lower iodine values than their non-conjugated forms. Thus the refractive index and iodine absorption curves indicate that under the conditions of polymerization the reaction proceeds in a uniform and characteristic manner.

Heretofore, little or no importance has been attached to the conditions of polymerization as they influence the reactions involved and the nature of the products formed.

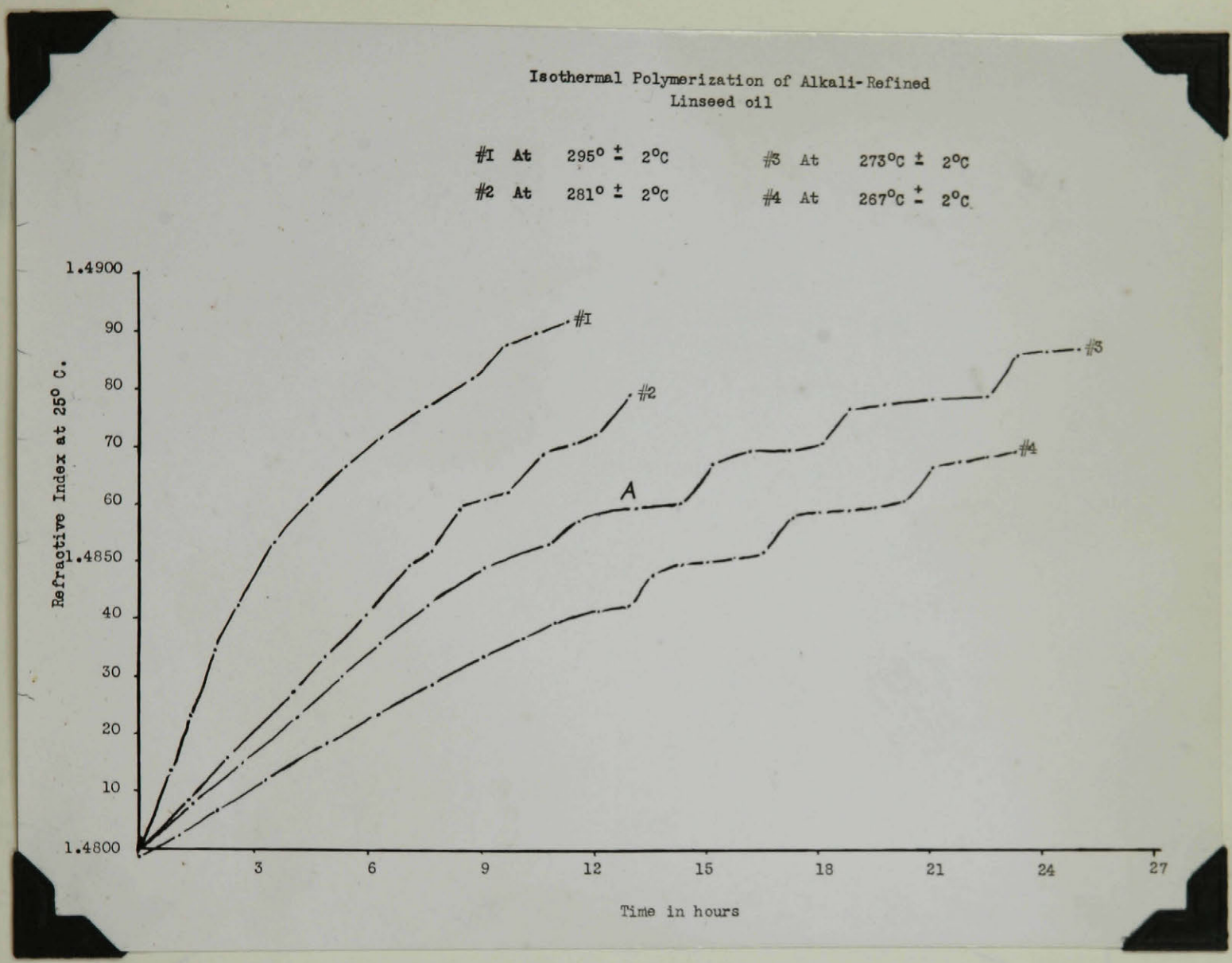


Figure 5 - Showing the relationship between refractive index and the time of polymerization of linseed oil at various temperatures.

#1 - Refractive index curve of polymerized linseed oil (270±½°C)

#2 - Iodine absorption curve of " " " "

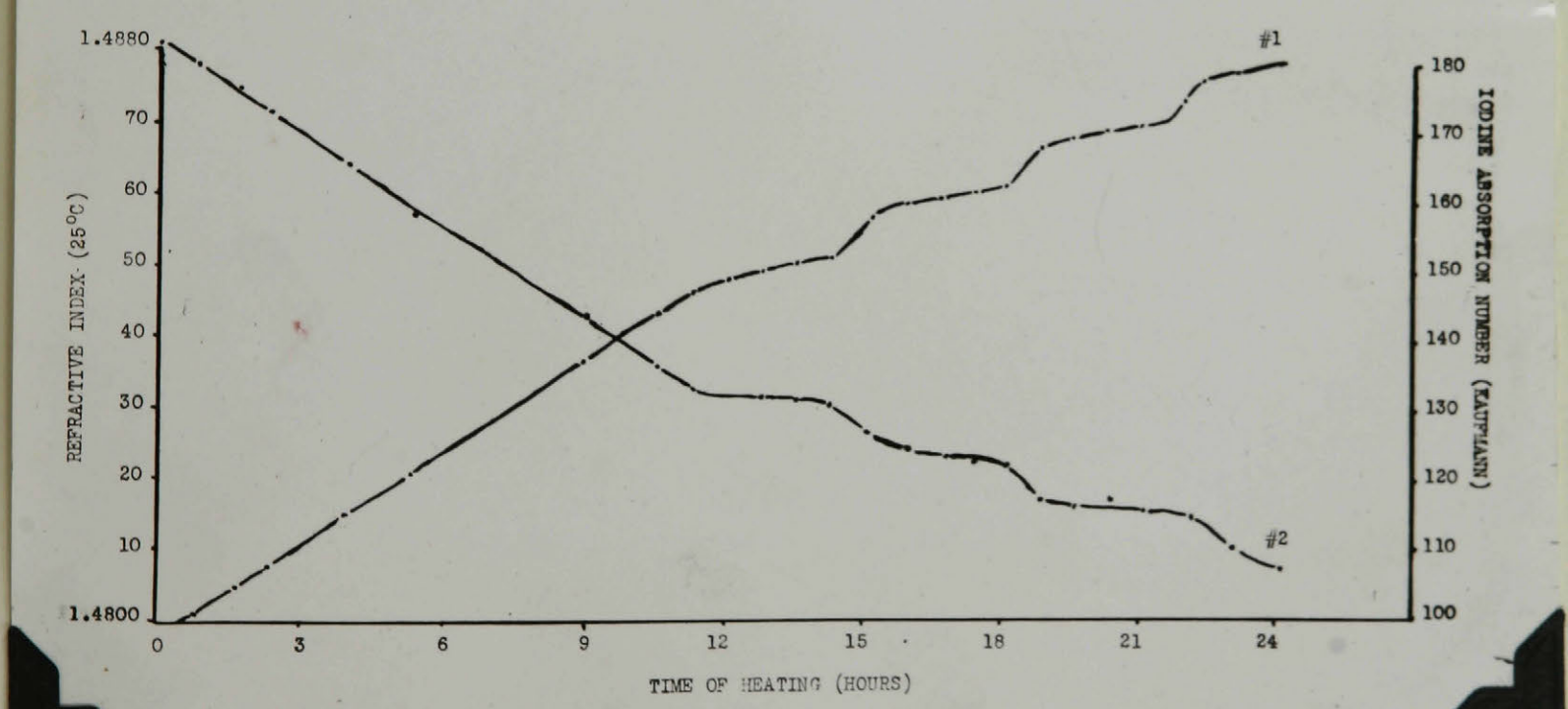


Figure 6 - Showing the relationship between the iodine number, refractive index and duration of polymerization of linseed oil at 270°C.

In industry, high temperatures (300°C and above) are employed to speed up the reactions, and the surface of the oil is blanketed with an inert gas. Under these conditions side reactions involving decomposition products are quite extensive and complicate the study of the primary polymerization. These side reactions are almost completely eliminated under the conditions of polymerization employed in these experiments and the analytical results are an expression of the primary polymerization reactions. The elimination of side reactions is accomplished by (a) low temperature polymerization and, (b) removal of decomposition as soon as formed, by bubbling carbon dioxide through the oil. These decomposition products probably consist chiefly of acids, aldehydes and perhaps ketones since they are highly acidic and reduce the Folin and Ciocalteu reagent (19) and potassium ferricyanide.

B. The Nature of the Primary Polymerization Reactions.

(1) Solvent segregation.

Batch extraction of three oils polymerized at 295-300°C., 275°C., and 270°C., respectively, was carried out according to the process previously described. The results are presented in Table I.

When the polymerization is carried out at high temperatures (above 295°C) more of the oil is extracted and

the soluble oil has correspondingly higher refractive index than when low temperatures are employed. For example, when the oil is polymerized at 295-300°C., and to a refractive index of 1.4859, 95% of the oil is soluble and this oil has a refractive index of 1.4850, whereas, under the same conditions of extraction but when polymerization is carried out at 275°C., and to a refractive index of 1.4859, only 60% of the oil is soluble and this oil has a refractive index of 1.4832 (see Table 1). When the polymerization is carried out at 270°C to the same refractive index the yield of acetone soluble oil is very much lower (45% vs 95%), than when the oil is polymerized at 295-300°C., and the refractive index is also correspondingly lower. In this case the extraction is carried out at a slightly lower temperature. Similar results with more highly polymerized oils may also be noted in Table 1.

These results indicate that at the high temperatures a larger portion of the oil is polymerized to a lower degree, whereas at the lower temperatures a smaller portion of the oil is polymerized to a higher degree. Thus, at the low temperatures the reactions are selective, the more reactive fraction of the oil being polymerized first. The stepwise nature of the refractive index and iodine absorption curves also indicates that the reactions are selective at lower

TABLE I - Results of Batch Extraction with Acetone of Thermally Processed Alkali-Refined Linseed Oil.

R.Index Linseed Oil (25°C)	Conditions of Polymerization		Analyses of Polymerized Oils			
	Temperature	Time (Hours)	Whole Oil R. Index (25°C)	Yield # (%)	Acetone Soluble Oil R.Index (25°C)	Acetone Soluble Oil Iodine Number (Kaufmann)
1.4795	295-300°C	4	1.4859	95	1.4850	-
		6	1.4872	78	1.4850	-
		10	1.4888	49	1.4850	-
1.4795	275°C	14	1.4859	60	1.4832	138.0
		12	1.4850	56	1.4822	136.3
1.4791	270°C	16	1.4861	45	1.4819	131.2
		20	1.4870	35	1.4816	127.2
		24	1.4881	27	1.4814	122.8

The acetone segregation of the oils polymerized at 295-300°C and 275°C was carried out at room temperature, but the oil polymerized at 270°C was segregated with acetone at 5°C.

temperatures and apparently take place in a series of intermittent stages.

Liquid-liquid extractions were carried out on four oils representing the four stages in the polymerization of linseed oil at 270°C corresponding to the four flat portions in the refractive index curve (Figure 6, curve 1). The multiple extraction unit was employed so that the four oils were extracted at the same time under identical conditions. The results presented in Table 2, show a definite trend in the refractive indices of successive extract cuts in relation to the time of extraction. The oil consists of three distinct fractions:

(i) a readily extracted fraction,
(ii) a fraction which is extracted very slowly, in 12 hours of more, and corresponds to a rise in refractive index, and
(iii) a highly insoluble portion which remains in the extractor.

These fractions represent various degrees of polymer formations. The first fraction, which has a low refractive index, is non-polymeric in nature as it contains no dibasic acids (Table 4). The second fraction has undergone initial polymer formation but it is not so cpmplex that it is insoluble, while the last fraction, since it has a very high refractive index, a high viscosity and a high content of dibasic acid, is highly polymerized. The decrease in the percentage of the non-polymeric fraction corresponding

TABLE 2 - Yield and Refractive Index of Segregates Obtained By Continuous Liquid-liquid Extraction at 20°C of Four Samples Representing Four Stages in the Heat Polymerization of Linseed Oil

Segregate No.	Stage I (approx.13 hrs.at 270°C)			Stage II (approx.17 hrs.at 270°C)			Stage III (approx.21 hrs. at 270°C)			Stage IV (approx.25 hrs. at 270°C)		
	Extraction Time (hours)	Yield (%)	R. Index (25°C)	Extraction Time (hrs.)	Yield (%)	R. Index (25°C)	Extraction Time (hrs.)	Yield (%)	R. Index (25°C)	Extraction Time (hrs.)	Yield (%)	R. Index (25°C)
1	5.5	56.0	1.4825	3.5	39.3	1.4822	1.5	25.7	1.4817	1.0	11.0	1.4814
2	7.5	5.4	29	4.5	8.7	24	2.5	10.5	20	2.0	9.0	17
3	9.5	4.6	30	5.5	4.5	27	4.5	7.6	24	3.0	9.0	20
4	10.5	3.0	32	7.5	5.5	30	5.5	5.0	32	4.0	8.5	24
5	13.5	5.7	41	9.5	5.9	40	7.0	2.1	39	5.0	5.5	34
6	25.0	5.4	60	11.0	2.0	48	9.0	2.1	48	6.0	2.0	40
7				12.0	4.5	60	12.0	3.8	58	8.0	2.5	48
8				24	8.5	90	24.0	5.0	73	10.0	1.5	59
9								6.3	98	13.0	3.5	70
10										22.5	4.0	92
Residual Oil (Insol.)	25.0	19.8	1.4930	24.0	24.9	1.4940	24.0	31.6	1.4942	22.5	43.2	1.4942

to a progressive increase in the highly polymerized fraction from the first to the fourth stage, thus indicating that the polymerization takes place in a definite sequence of reactions. Since there is a progressive decrease in the refractive index and diene conjugation value (Figure 9) of the non-polymeric fractions, from the first stage to the fourth stage, it appears that the more highly unsaturated glycerides are polymerized most readily and hence are removed from the non-polymeric fractions.

(1) Ultraviolet Absorption Studies.

To elucidate the nature of the reactions taking place at the lower temperature the ultraviolet absorption spectra of various fractions was studied. The light absorption of many samples was measured over a range of wave lengths from 2240 to 3200 Å but the only maxima found was that for diene conjugation which is measured at 2320-2340 Å (Figure 7). The results with samples polymerized at 270°C (Figures 7 and 8), show a marked increase in diene conjugation in the initial period of polymerization. This has already been observed by a number of workers (10,34,11). Diene conjugation appears to reach a maximum about the ninth hour of polymerization, remains relatively constant for the next five hours and then decreases gradually. This maximum has also been

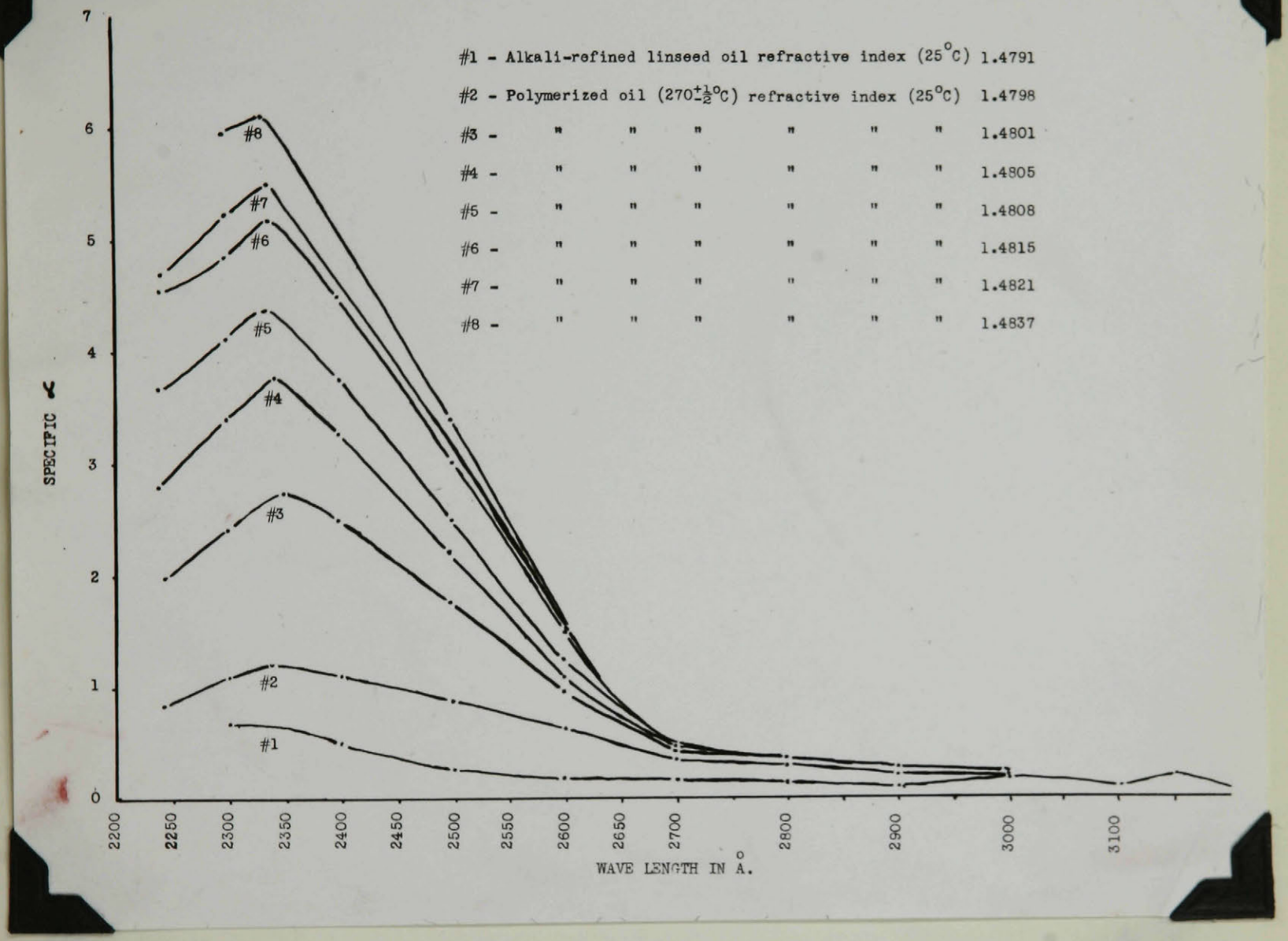


Figure 7 - The ultraviolet absorption spectra of oils at various stages in the initial period of the polymerization of alkali-refined linseed oil.

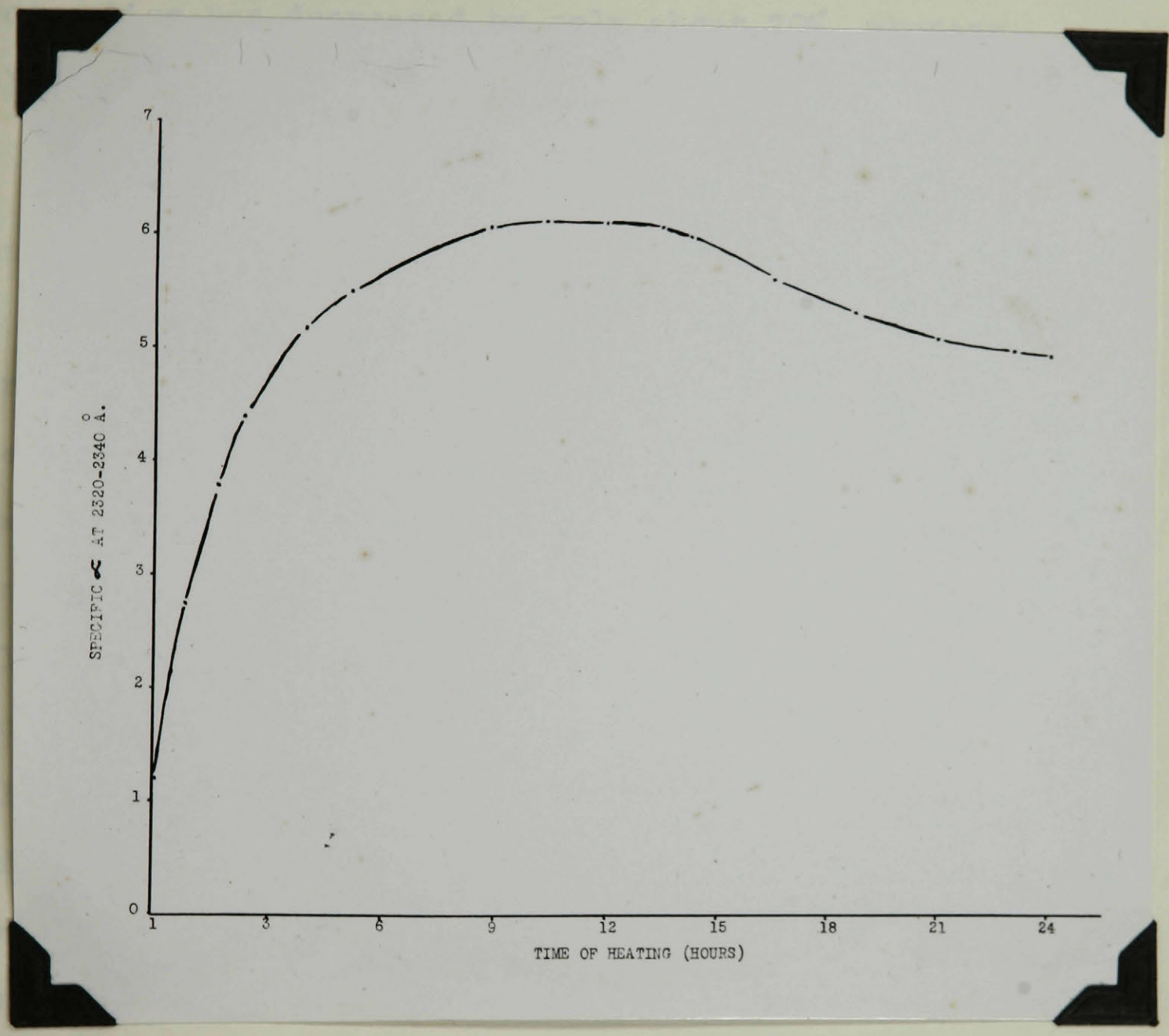


Figure 8 - Showing the relationship between the extent of diene conjugation (measured at 2320-2340 Å) and the time of heating alkali-refined linseed oil at 270 ± 0.5°C.

observed by Bradley and Richardson (10), who believe that an equilibrium is established where diene conjugation is being used up in polymer formation as rapidly as it is being formed. However, at the twenty-fourth hour diene conjugation has decreased by only about 20%, whereas polymerization has proceeded to a much greater extent.

There must, therefore, be further conjugation of double bonds after primary polymerization, otherwise the decrease in diene conjugation would parallel the increase in polymerization. This is further supported by analysis of the acetone segregates (Table 3). The results show that the low polymer fractions (7,8, and 9) (Table 3) are very highly conjugated. Since these oils have undergone primary polymerization, further conjugation of the remaining double bonds must have taken place. However, as the molecules become more complex, as indicated by the increase in refractive indices and decrease in the solubility in acetone, the extent of diene conjugation diminishes. It appears, therefore, that in both primary and secondary polymerization of the triglyceride molecules a shift of double bonds into a diene conjugate system is involved.

Analyses of the acetone soluble, non-polymerized oils (Figure 9) show that the diene conjugation is highest in the fraction segregated from the oil polymerized to the first stage and lowest in the oil polymerized to the fourth stage. The acetone-insoluble oils also show this same relationship (Figure 10).

TABLE 3 - Showing the relationship between diene conjugation and the complexity of the polymers.

(Segregation by liquid-liquid extraction with acetone at 20°C of the second stage oil polymerized at 270 ± 0.5°C.)

Segregate No.	Refractive Index (25°C)	Acetone-Soluble Oil Yield (%)	Diene Conjugation (Specific Absorption at 2320 -2340 Å)
1	1.4821	6.2	6.3
2	1.4821	5.5	-
3	1.4822	5.4	-
4	1.4822	9.3	-
5	1.4822	12.9	5.6
6	1.4824	8.7	-
7	1.4829	4.5	6.4
8	1.4830	5.5	6.7
9	1.4840	5.9	6.7
10	1.4848	2.0	-
11	1.4860	4.5	6.5
12	1.4890	8.5	5.8
13#	1.4940	24.9	5.7

Insoluble in acetone.

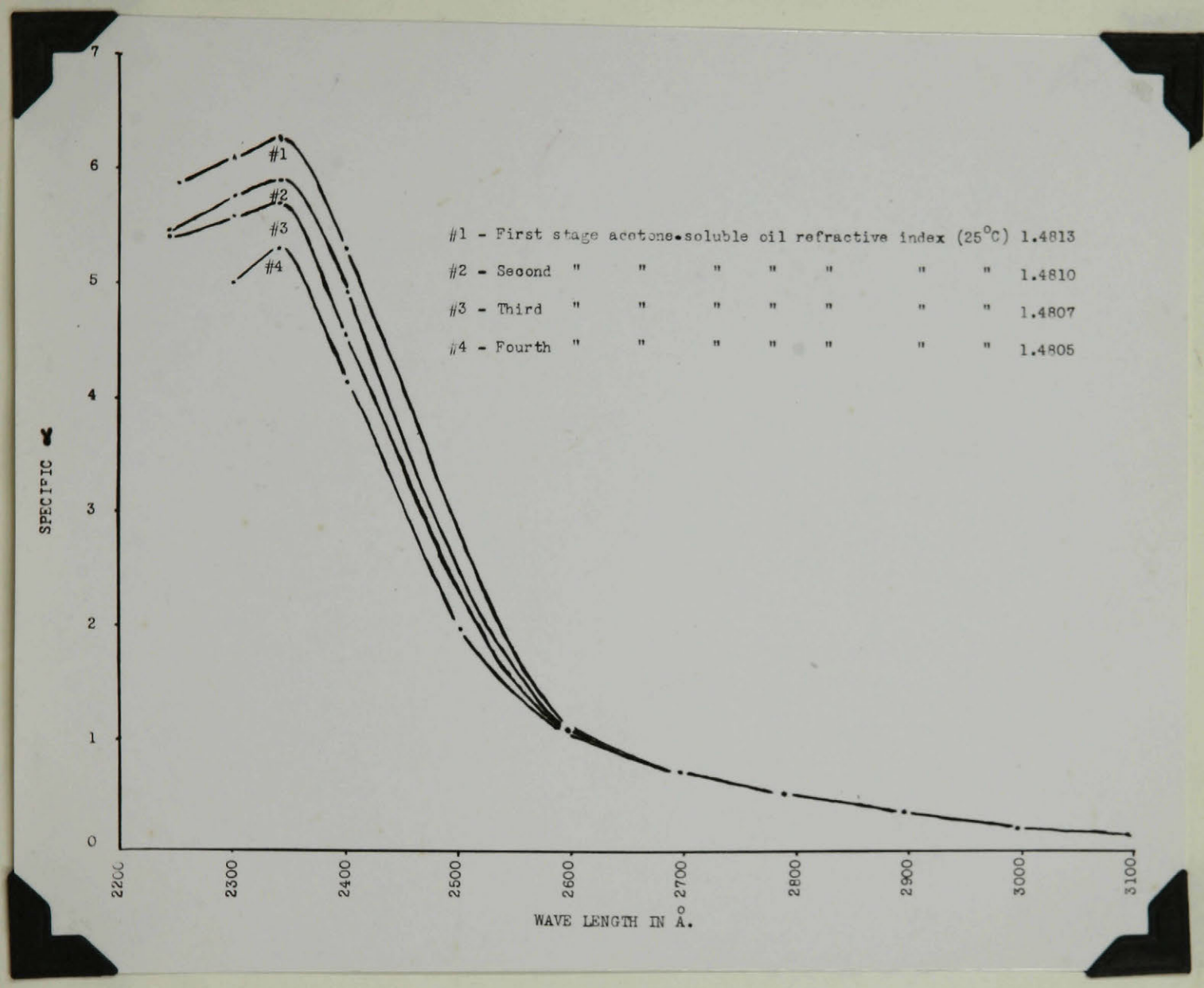


Figure 9 - Ultraviolet absorption spectra of the non-polymer, acetone-soluble oils of four stages of an oil polymerized at 270 ± 0.5°C.

Yields of acetone-soluble oil.

#1. 30.8% of original polymerized oil.
#2. 28.4% " " " "
#3. 21.4% " " " "
#4. 14.5% " " " "

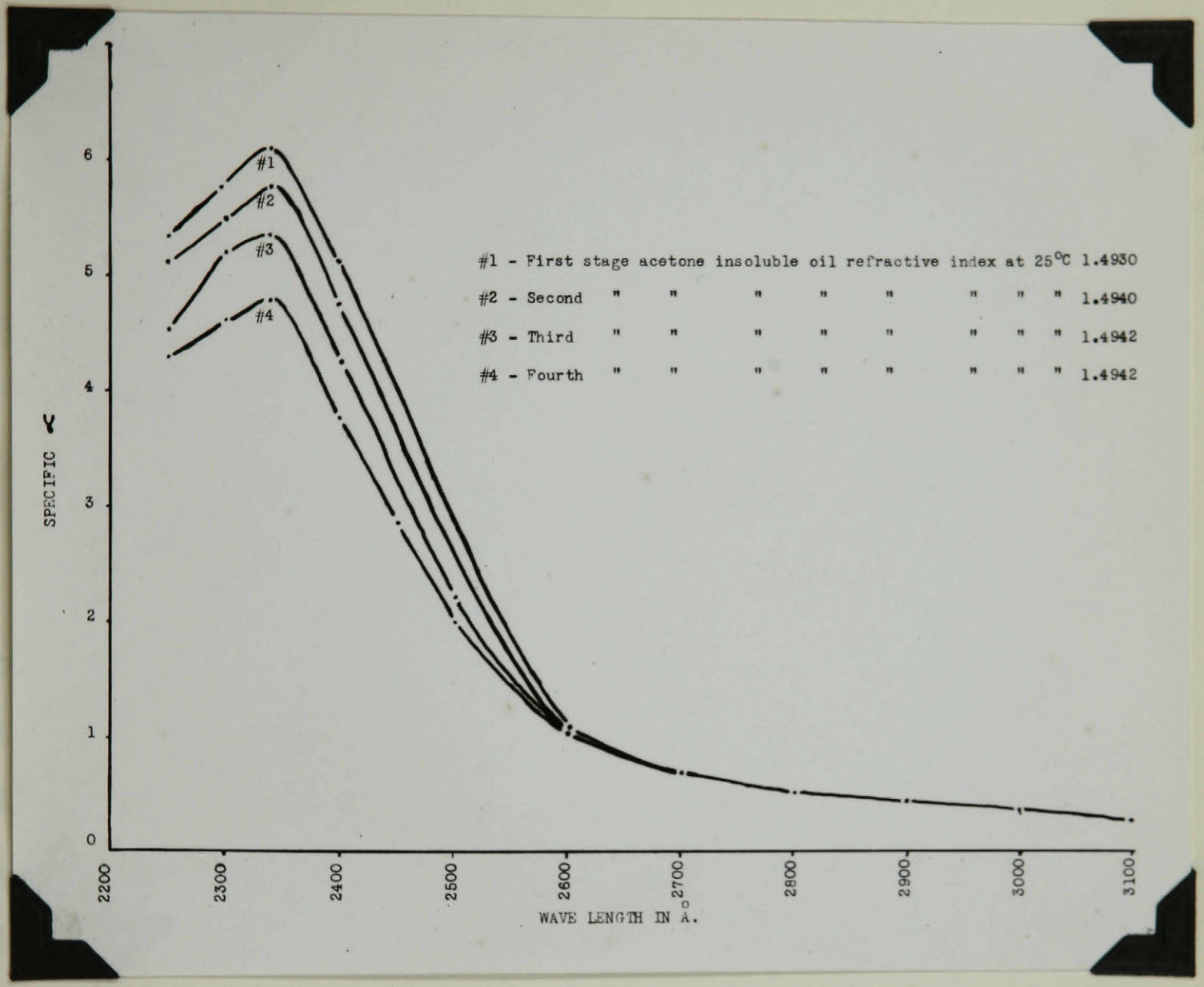


Figure 10 - The ultraviolet absorption spectra of the acetone-insoluble oils of four stages of an oil polymerized at 270 ± 0.5°C.

Yields of acetone-insoluble oil.

#1. 19.8% of original polymerized oil.
#2. 24.9% " " " "
#3. 34.4% " " " "
#4. 43.4% " " " "

Since the diene conjugation values, iodine values and refractive indices are higher for the non-polymerized fraction of the first stage oil, it is suggested that this fraction consists of more highly unsaturated glycerides than are contained in the non-polymerized fraction of the oils at the other stages of polymerization. If this is true, polymerization must have proceeded in a selective manner according to the level of unsaturation in the triglyceride molecule.

(3) Fractionation of the Fatty Acids.

To obtain further evidence for the selective nature of the polymerization a fractionation of the fatty acids of the acetone-soluble, acetone-insoluble and whole polymerized oils was carried out. The results (Table 4) are in agreement with the above postulate, in that the acetone-soluble oils contain a much higher percentage of solid acids than the original oil and the highly polymerized insoluble oils contain only traces of a solid acid fraction. The highest percentage of solid acids is expected in the acetone-soluble oil of the fourth stage since, according to the above theory, as the polymerization proceeds the more highly unsaturated triglycerides are polymerized first and hence removed. Apparently the acetone-soluble oils do not contain polymers since dibasic acids are absent.

Polymerized at 270°C for Varying Periods of Time.

Sample	Stage of Polymerization	Solid Acids Yield#	Solid Acids Iodine Absorption No. (Kaufmann)	Unsaturated Acids R.Index (35°C)	Unsaturated Acids Yield# (%)	Unsaturated Acids Iodine Absorption No. (Kaufmann)	Dibasic Acid Fractions R.Index (35°C)	Dibasic Acid Fractions Yield# (%)	Dibasic Acid Fractions Iodine Absorption (Kaufmann) ##
Original Polymerized Oil	(1	8.0	65.4	1.4697	62.5	159.0	1.4836	20.6	140.5
	(2	8.2	-	1.4698	59.0	156.3	-	23.3	135.2
	(3	8.3	68.7	1.4699	58.7	153.2	1.4855	26.7	130.9
	(4	8.5	73.4	1.4699	55.2	147.2	1.4885	28.9	128.2
Acetone-Soluble Oil	(1	10.6	65.4	1.4700	80.4	160.5			
	(2	13.4	68.6	1.4698	80.6	157.0			
	(3	-	68.7	1.4695	75.7	152.8			
	(4	18.3	70.4	1.4690	72.4	150.3			
Acetone-Insoluble Oil	(1	-	-	1.4697	61.7	144.0	1.4900	30.1	130.3
	(2	-	-	1.4697	56.0	142.8	1.4908	39.4	129.8
	(3	Trace	-	1.4700	43.4	141.0	1.4900	48.0	130.0
	(4	Trace	-	1.4704	40.5	139.1	1.4902	54.8	128.2
Linseed Oil (Untreated alkali-refined)		8.6	3.5	1.4667	84.3	195.8			

Yields are expressed as percentage of original sample and not as percentage of total acids which comprise about 95% of the glycerides.

0.32 N. bromine reagent was used.

The percentage of acids whose lead salts are insoluble in 95% ethyl alcohol would be expected to increase as polymerization proceeds since more dibasic acids are produced. However, as mentioned previously, the low molecular weight of these acids in the whole oil as compared to the acids isolated from the acetone-insoluble oils indicates some contamination with monobasic acids.

Although the percentage of acetone-insoluble oil at the first stage of polymerization is considerably less than at the fourth stage, the refractive indices are about the same. This indicates that they are corresponding fractions (Table 5).

TABLE 5 - Analyses of High Polymer Acetone-Insoluble Oils.

(Alkali-refined linseed oil, refractive index 1.4791 at 25°C polymerized at 270 ± 0.50°C., liquid-liquid extracted 24 hours).

Stage of Polymerization	Whole Oil R. Index (25°C)	Acetone-insoluble Oils			
		R.Index (25°C.)	Yield (%)	Dibasic Acids (%)	Molecular Weight
1	1.4850	1.4930	19.8	30.1	1560
2	1.4860	1.4940	24.9	39.4	-
3	1.4870	1.4942	34.4	48.0	2030
4	1.4880	1.4942	43.4	54.8	2610

The large increase in the percentage of dibasic acids in this fraction at the fourth stage as compared to the first

stage is very significant. These fractions, therefore, must be of widely different constitution. This is also supported by the difference in diene conjugation (Figure 10), and molecular weights (Table 5). The molecular weights indicate that the predominant structure of the acetone-insoluble fraction at the first stage is a dimer and in the subsequent stages, mixtures of dimers, trimers and perhaps tetramers. However, the percentage of dibasic acids present in these fractions indicate that these are not simple molecules and that considerable intramolecular reactions must have taken place. It appears, therefore, that the most highly unsaturated triglycerides, followed by those of lesser unsaturation, polymerize in a succession of reactions through the formation of dimers, trimers, tetramers and so on until gelation occurs.

The yield and iodine value of the unsaturated acids of the whole polymerized oil and of the acetone-soluble oil decreases as polymerization proceeds from the first to the fourth stage. This would be expected since polymerization involves only the unsaturated acids. No linolenic acid is present in any of these processed oils as indicated by a negative hexabromide test. The iodine values of the unsaturated acids, however, do indicate the presence of some octadecatrienoic acid. Notwithstanding the fact that linolenic acid is more susceptible to polymerization than linoleic or oleic acid some isomer of this acid must

be present. This further supports the foregoing postulate as some of the lesser unsaturated glycerides would contain some octadecatrienoic acid according to Hilditch's theory regarding the equal distribution of the fatty acids in the glyceride molecule (22).

(4) Chromatographic studies.

An attempt was made to segregate the component triglycerides of the acetone-soluble oils by adsorption on a column of activated aluminium oxide. Acetone-soluble oils of the first, second and fourth stages of polymerization were analyzed (Table 6). According to Walker and Mills (54), the most highly unsaturated triglycerides are absorbed at the top of the column. It was found that the oils could be separated into two fractions; one was readily washed through the column with Benzin and the other was eluted very slowly by Benzin but very readily with diethyl ether. Although the refractive indices and iodine values of the various component triglycerides of linseed oil have been reported (54), these values cannot be applied here, since the component triglycerides of these oils are very highly conjugated (Figure 9), and the refractive index and iodine absorption are greatly influenced by conjugation. However, the difference in the refractive index of the adsorbed oil and the eluted oil indicates that separation of the most highly unsaturated triglycerides was achieved.

TABLE 6 - Chromatographic Analyses of Acetone-soluble Oils Obtained by Batch Extraction of Linseed Oil Polymerization at 270 ± 0.5°C.

	Stage 1		Stage 2		Stage 4	
Benzin Eluant	R.Index (35°C)	Iodine Number (Kaufmann)	R.Index (35°C)	Iodine Number (Kaufmann)	R.Index (35°C)	Iodine Number (Kaufmann)
1	1.4750	141.2	1.4745	137.1	1.4740	128.3
2	1.4753	140.3	1.4750	-	1.4750	-
3	1.4753	-	1.4750	-	-	-
4	1.4758	-	1.4754	-	-	-
5	1.4760	-	-	-	-	-
6	1.4770	-	1.4772	-	1.4775	-
Diethyl Ether	1.4820#	140.5	1.4810	135.0	1.4810	116.7

Stage 1 - Acetone-soluble oil = 55% of original oil

Stage 2 - " " " = 44% " " "

Stage 4 - " " " = 28% " " "

Molecular weight of this fraction is 860.

The slight decrease in iodine value during the course of elution, particularly in the case of acetone-soluble oils, stage 1 and stage 2, is probably due to the influence of conjugation on the method of determination. Since the most unsaturated fraction (adsorbed strongly and eluted with ethyl ether) is highly conjugated, the iodine absorption values are low, whereas the iodine absorption values of the more saturated fraction give a more reliable indication of the degree of unsaturation. The difference, however, in the iodine values and the refractive indices of the adsorbed oils (fraction eluted with ether) indicates that the most highly unsaturated fraction of stage 1 has a higher degree of unsaturation than that of stage 4. This would only be expected if the polymerization had proceeded according to the level of unsaturation in the triglyceride molecule. Although the technique used in the preparation and elution of these columns was essentially the same, the results indicate that the chromatogram was more fully developed in the case of the acetone-soluble oil obtained from the fourth stage of polymerization. The probable explanation is that the more saturated oil facilitated elution of the unsaturated glycerides with Benzin under the same conditions.

II - PRODUCTION OF A "NON-REVERTING" SHORTENING

A. Polymerization and Solvent Segregation.

Since the problem of flavour reversion is encountered in hydrogenated linseed and soybean oils and not in sunflower and cotton seed oils, it appears that "reversion" is in some way associated with the linolenic acid which comprises about 40% of linseed oil and 6% of soybean oil and is not present in the latter oils. Lemon (30) postulated that the linolenic acid is saturated first at the Δ 12, 13 double-bond to form an isomer of the common linoleic acid which, when heated, gives rise to the odoriferous product. Armstrong and McFarlane (1) heated the oil at 230°C for 12 hours under an atmosphere of hydrogen but the quality of the shortening obtained was not improved. However, with a higher temperature and with carbon dioxide bubbling through the oil during the heating period, volatile obnoxious products were eliminated and the shortening obtained did not revert.

Since the presence of the polymerized fraction in the finished shortening is undesirable, the oil was segregated with acetone to extract this fraction. Hence a process, based on heat polymerization and solvent segregation, was developed for the production of a non-reverting shortening from alkali-refined linseed oil, the first step being the polymerization of the alkali-refined linseed oil.

The temperature at which the polymerization is carried out is especially important in obtaining the desired oil for the preparation of shortening. If polymerization takes place at temperatures above 280°C or at temperatures so low that the period of heating is unduly prolonged, the shortenings obtained are of poor quality. Some improvement is obtained by using the acetone-soluble fraction of these polymerized oils but they still do not make good quality shortenings. The best oil is obtained by heating at 270-275°C for 12-15 hours. At this stage (A, Figure 5) the whole oil has a refractive index of 1.4858 - 1.4861 and when segregated at room temperatures yields 60-65% of acetone-soluble oil which has a refractive index of 1.4830 - 1.4834 (25°C). If the segregation is carried out at 5°C the yield is about 10% lower and the refractive index is 1.4800 - 1.4804 (30°C). The refractive index of the original polymerized,oils and the acetone-soluble fraction of these oils, will vary to some extent, depending on the value for the original alkali-refined linseed oil.

The continuous passage of carbon dioxide is an essential condition in the process as it eliminates volatile decomposition products, including free acids. The oil is characterized by a low acid value (0.5-1% as oleic acid) and a pale yellow colour. The latter is a criterion of the efficiency with which the decomposition products have been removed. The volatile products represent about 5% of the

original oil. If the oil is simply heated under carbon dioxide the acid value of the product may be as high as 12% (as oleic acid) and obviously it will contain all the decomposition products. The shortenings obtained from such oils are of very poor quality. As previously mentioned, a small portion, about 4%, of the polymerized oil is soluble in 95% methanol at room temperature. This oil has a fishy odour and a deep brown colour, and apparently constitutes a fraction of the decomposition products which is not removed by the carbon dioxide treatment. Insofar as reversion is concerned no apparent advantage accrues from separating this fraction prior to acetone segregation.

B. Hydrogenation and Deodorization.

No special treatment is required in the hydrogenation of the processed oils and most of the commercial catalysts which were tested gave satisfactory results. The results reported in Table 7 were obtained with a catalyst consisting of reduced nickel on a silica-gel base (1). This catalyst is prepared according to Hilditch (21), except that silica-gel is used as the carrier instead of Kieselguhr. The course of hydrogenation at various temperatures as indicated by refractive indices is illustrated in Figure 11. The best shortenings were obtained by hydrogenating to a refractive index of 1.4615 - 1.4605 at 60°C (Table 7).

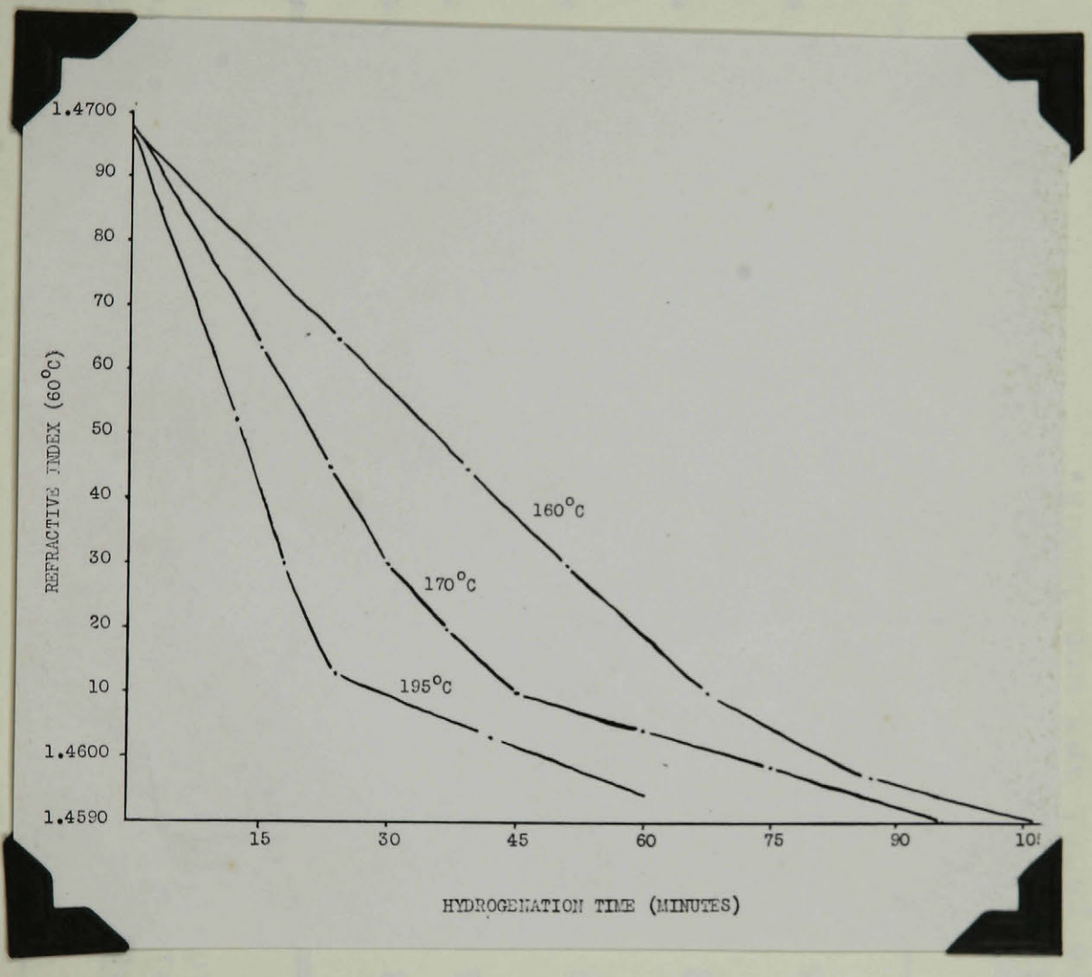


Figure 11 - Showing the relationship between the refractive index and the duration of hydrogenation of the acetone-soluble fraction of polymerized linseed oil.

TABLE 7 - Summary of Experimental Data on the Process for the Production of an Edible Shortening (Alkali-refined Linseed Oil, Refractive Index 1.4795, Polymerized at 272-275°C for 14 Hours; Hydrogenated at 170°C to Different Refractive Indices).

Run No.	Polymerized Oils: Whole Oil R.Index (25°C)	Acetone-Soluble Yield#	Acetone-Soluble R.Index (25°C)	Acetone-Insoluble Yield#	Acetone-Insoluble R.Index (25°C)	Shortenings: R.Index (60°C)	Color ##	Consistency	Judgement of Pastry: Flavour Reversion	Grade Compared to Controls
1	1.4859	60	1.4830	32	1.4890	1.4621	Slight yellow	Too soft	None###	Not so good
2	1.4860	62	1.4834	33	1.4892	1.4619	Very " "	soft	"	No discernible diff.
3	1.4859	63	1.4832	32	1.4889	1.4612	Pure white	Good	"	No discernible diff.
4	1.4858	63	1.4831	32	1.4890	1.4608	" "	"	"	Better than controls
5	1.4859	62	1.4830	33	1.4888	1.4604	" "	Slightly Hard	"	No discernible diff.

Percentage of original oil.
Not decolorized with adsorbent clays nor creamed.
The decision of the panel was unanimous.
Two commerical samples of shortening included as standard of reference.

The pastry was judged simultaneously for flavour, odour and texture by a panel of 10 judges made up of graduate dietitians, housewives and cooks.

The shortenings were deodorized for at least three hours using superheated steam at 180-200°C and 5 mm. pressure. It was sometimes necessary to refilter the shortenings after deodorizing so as to remove traces of catalyst which passed through in the first filtration and imparted a dark colour to the shortenings. The data obtained in five typical runs are summarized in Table 7.

C. Toxicity and Pancreatic Lipase Studies.

Toxicity tests were carried out on both the acetone-soluble oil and the alcohol-acetone segregated oil. There appeared to be no difference in the behavior of these two oils. Two toxicity tests were made, the first with nine-week old rats (Table 8), and the second with five-week old rats (Figure 12).

There was no evidence of skin lesions or diarrhoea and the rats' coats possessed the healthy lustre expected with a high fat diet. The oils were almost completely odourless and tasteless yet the feed intake was low indicating perhaps that the oils were not palatable. In the second test the addition of molasses on the fifteenth day appeared to have some affect. However, the subnormal growth may have been due to small amounts of toxic substances in the shortenings.

TABLE 8 - Results of First Toxicity Test With Rats.

Sample	R.Index (25°C)	Initial Body Weight in Grams	10th Day	Gain	Feed Consumption Grams
Linseed Oil (Alkali-Refined)	1.4791	125	135	10	113
		136	153	17	141
		148	190	42	177
		160	188	18	151
		139	159	20	167
Acetone-Soluble Oil	1.4820	170	193	23	144
		167	165	-2	120
		135	135	0	116
		134	139	5	102
		175	177	2	121
Alcohol-acetone Segregated Oil	1.4820	178	207	29	170
		179	179	0	125
		126	139	13	142
		151	150	-1	139
		126	135	9	123

Note: The group of rats on the linseed oil diet and the first rat in each of the other groups had previously been fed a vitamin A deficient diet. Thus, although they showed no vitamin A deficiency symptoms when they were put on test, the large gains may be due in part to vitamin A.

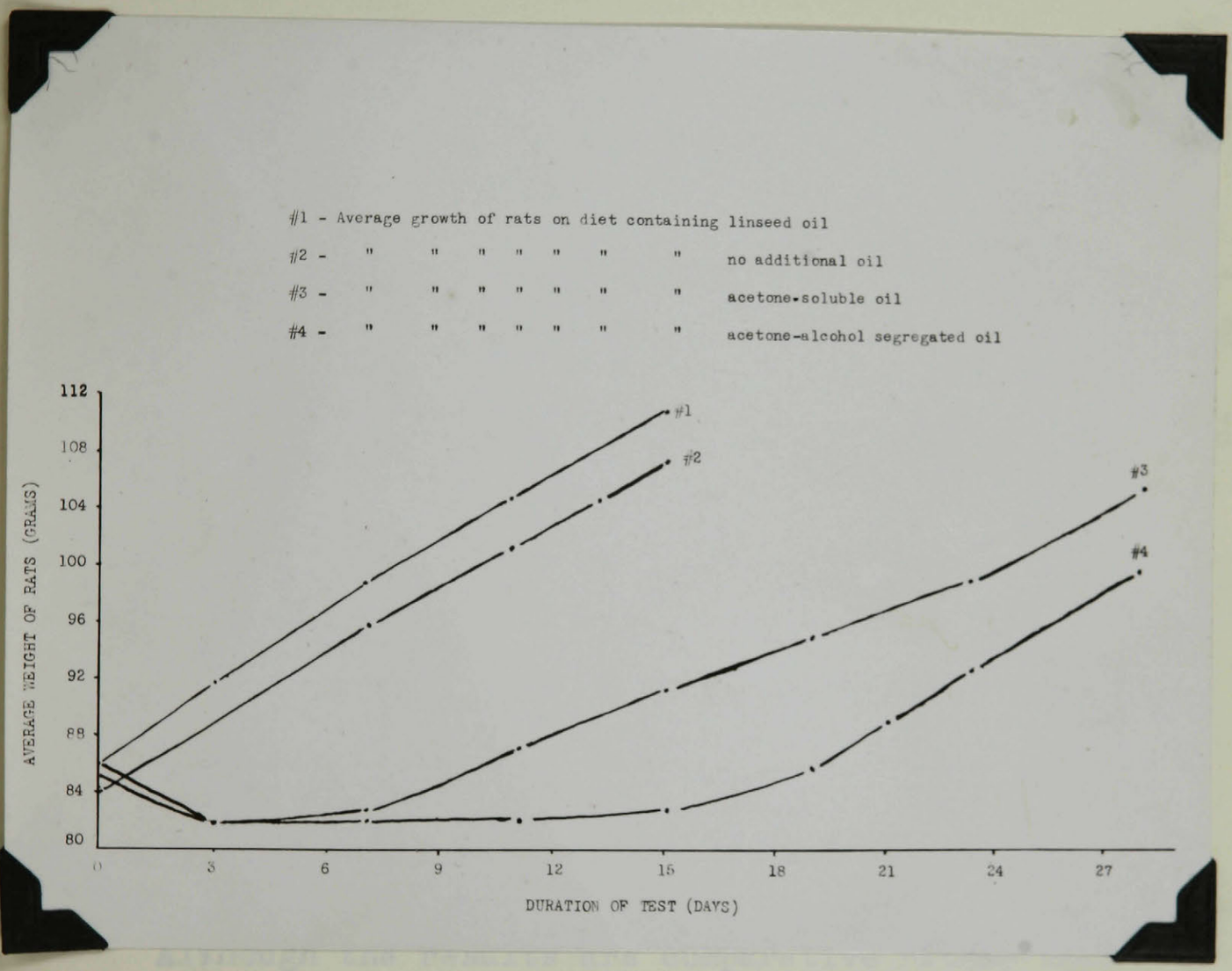


Figure 12 - Results of second toxicity test. At the 15th., day the diet was flavoured with about 1% molasses.

Average weight of feed consumed over a 15-day period:-

Group 1 - 155 grams
Group 2 - 159 "
Group 3 - 120 "
Group 4 - 115 "

The action of pancreatic lipase on these oils was studied to determine if they might be resistant to enzymatic hydrolysis in vitro. The results are shown in Table 9.

TABLE 9 - Results of Tests of Activity of Pancreatic Lipase with Polymerized Oils as Substrate.

Substrate	Degree of Hydrolysis at Varying Times (Results expressed in ml.0.1N.N_aOH)		
	25 min.	50 min.	106 min.
Linseed Oil	7.4	10.7	17.3
" "	7.4	10.7	15.8
Acetone-soluble Oil	10.6	10.3	12.0
" " "	10.2	10.8	12.1
Olive Oil	10.1	10.9	16.2
" "	9.8	11.2	15.8

Although the results are comparative rather than absolute, they indicate that the rates of hydrolysis of the acetone-soluble oils, untreated linseed and olive oils, are approximately the same.

III - PRODUCTION OF AN IMPROVED DRYING OIL

The drying of oils to form tough, adherent, impervious films involves both polymerization and oxidation. Since the reactions involve unsaturated double bonds, the film-forming properties are closely related to the degree of unsaturation. If, however, the polymerization process is initiated by heating the oil prior to mixing into paint, the drying time is accordingly shortened.

The polymerized fraction of the oil, segregated out in the process for the production of an edible shortening, comprises as much as 40% of the original oil. Since it corresponds to the more unsaturated fraction of the original linseed oil it s value as a paint and varnish oil was studied. Under the conditions of polymerization the oil has a pale yellow colour which is a very important factor, particularly in the manufacture of light coloured paints. The acid value is less than 1% which is also important, for example, in the manufacture of certain types of enamels.

It was found that the polymerized fraction can be further segregated by means of acetone into a number of oils of different viscosities or bodies from K to Z_6 Gardner units. Since oils of varying viscosities are desired by the drying oil industries these oils can be used for various purposes. In preliminary studies tests were conducted on oils which had been polymerized at 265, 270 and 275°C, and solvent segregated to obtain fractions showing a range of viscosities.

The results (Table 10) show that the temperature of polymerization has no influence on the drying properties, and although there is a wide range of viscosities, there is no difference in the drying times when no driers are added. The difference in drying time between the processed oils and the commercial sample is also not considered significant. The processed oils also compare favourably in other respects with the commercial oil and, with one exception, are greatly superior in color (Table 10).

To carry out a more extensive study, a larger sample of oil was polymerized at 270 ± 0.5°C., and fractionated by the batch process according to the following scheme: -

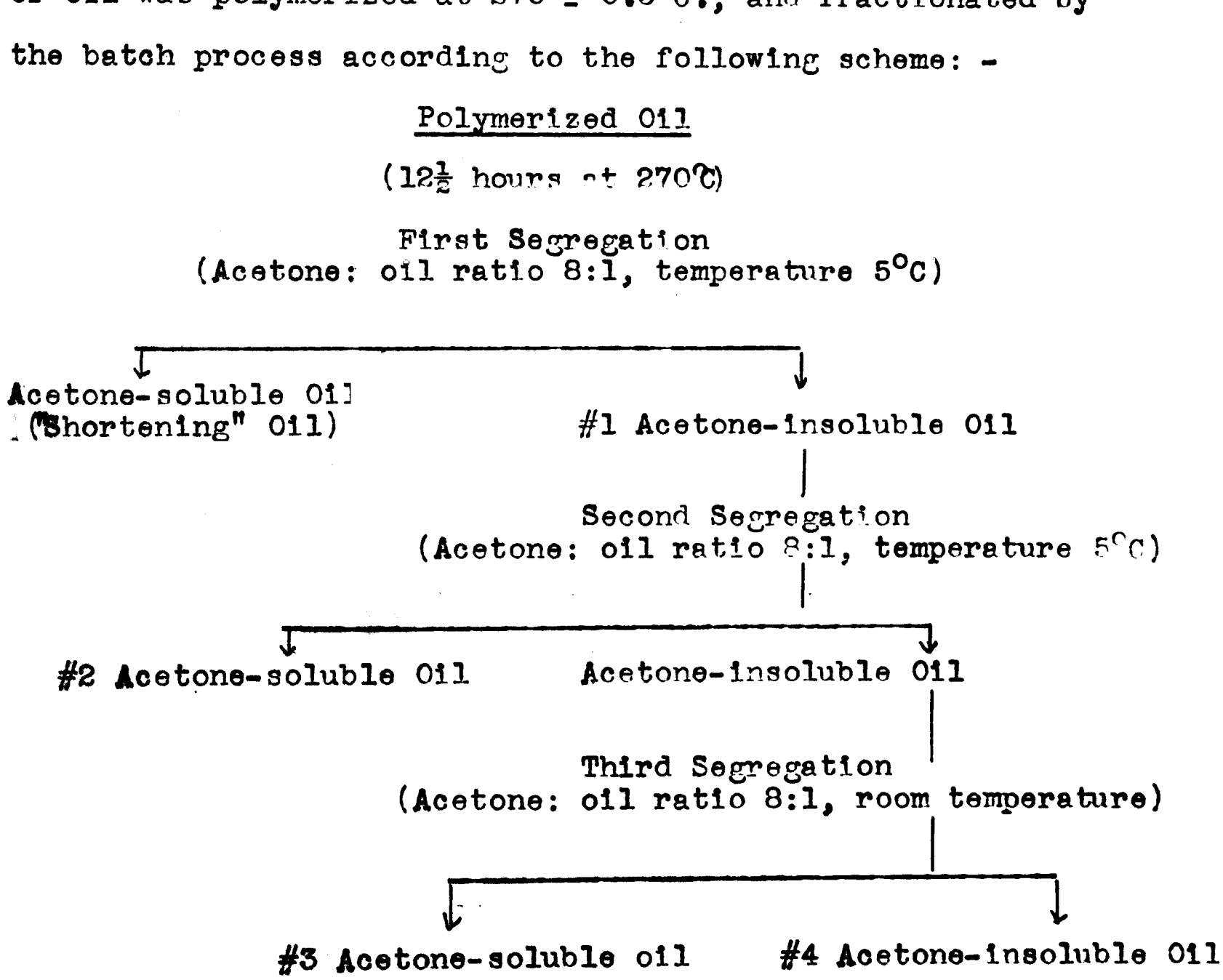


TABLE 10 - Properties of Drying Oils Prepared by Acetone Segregation of the Polymerized Oil

Polymerization Temperature	Time (Hours)	Acetone Segregation Number	R.Index (30°C)	Colour#	Body#	Drying Time (Hours)	Tolerance Mineral Spirits	Appearance
265°C	15	2.Insoluble (Room temp.)	1.4882	2	Y-Z	94	Very High	Excellent
		2.Soluble (Room temp.)	1.4842	6	R^+	94	Very High	Excellent
270°C	13	1.Insoluble (5°C)	1.4872	2	X	94	Very High	Excellent
		2.Insoluble (Room temp.)	1.4900	3	Z_1	94	Very High	Excellent
		2.Soluble (5°C)	1.4840	2	S	94	Very High	Excellent
275°C	11	3.Soluble (5°C)	1.4856	2	V	94	Very High	Excellent
		3.Insoluble (5°C)	1.4888	2	$Z_1 - Z_2$	94	Very High	Excellent
		4.Insoluble (5°C)	1.4920	3	$Z_4 - Z_5$	94	Very High	Excellent
Commercial, Polymerized, Solvent-extracted Oil				6-7	$Z_3 - Z_4$	86	Very High	Very Good

- See Table 11 for absolute values.

TABLE 11 - Relationship Between Gardner-Holdt Units for Viscosity, Gardner Units for Colour and Their Respective Absolute Values.

Viscosity		Colour	
Gardner-Holdt Units	Poises	Gardner Units	Gram of Potassium dichromate per 100 ml. concn. H_2SO_4
Q	4.35	1	0.0039
R	4.70	2	0.0048
S	5.0	3	0.0071
T	5.5	4	0.0112
U	6.27	5	0.0205
V	8.84	6	0.0322
W	10.70	7	0.0384
X	12.9	8	0.0515
Y	17.6	9	0.0650
Z	22.7	10	0.0780
Z_1	27.0	11	0.1640
Z_2	36.2	12	0.250
Z_3	46.3	13	0.572
Z_4	63.4	14	0.763
Z_5	98.5	15	1.041
Z_6	148.0	16	1.280

The results (Tables 12, 13) show that oil #4 is the best paint and varnish oil and is superior in all respects to the commercial polymerized, solvent-extracted oil as a varnish ingredient. The acid value of this oil is less than 0.5% as oleic acid and, hence, is far below the upper limit allowed by government specifications. This is important in the manufacture of paints and varnishes as the tendency to "liver up" is reduced to a minimum. The term "liver up" is used by the paint and varnish chemist to denote the formation of solid clumps or particles which are formed by the interaction of metal driers and pigments (e.g. zinc oxide) with free acids. For the manufacture of paints and varnishes, oils of a high body are preferred. However, in the leather and the protective coating industries oils with a low body combined with fast drying and low colour index are desirable. Hence, oil #4 would be most desirable for the manufacture of paints and varnishes, whereas oil #3 would be preferred by the leather and protective coating industries.

As has been indicated previously, liquid-liquid extraction can also be employed for solvent segregation and oils with a wide range of properties can be obtained. The non-polymeric fraction of the oil is extracted readily. The polymeric fraction of the oil is segregated on the basis of molecular complexity. The low viscosity fraction is extracted slowly and the highly viscous portion is insoluble

TABLE 12 - Drying Properties After Addition of Metal Driers to Oils Prepared by the Acetone-Segregation of Polymerized Oil.

Oil	Refractive Index (30°C)	Body Gardner-Holdt Units	Metal Naphthanate Drier (% Metal)	Drying Time		
				7½ Hours	16 Hours	17 Hours
1	1.4860	W-X	(0.10 Mn 0.08 Co	Tacky	Dry	
			(0.24 Pb 0.03 Co	Tacky	Almost dry	Dry
			(0.20 Pb 0.02 Mn	Tacky	Almost dry	Dry
2	1.4822	K-L	(0.10 Mn 0.08 Co	Tacky	Almost dry	Dry
			(0.24 Pb 0.03 Co	Tacky	Almost dry	Dry
			(0.20 Pb 0.02 Mn	Tacky	Almost dry	Dry
3	1.4840	U	(0.10 Mn 0.08 Co	Almost Dry	Dry	
			(0.24 Pb 0.03 Co	Tacky	Almost dry	Dry
			(0.20 Pb 0.02 Mn	Tacky	Almost dry	Dry
4	1.4916	Z_4-Z_5	(0.10 Mn 0.08 Co	Almost Dry	Dry	
			(0.24 Pb 0.03 Co	Tacky	Dry	
			(0.20 Pb 0.02 Mn	Tacky	Dry	

#-Samples designated "almost dry" may be considered "dry" after another hour.

TABLE 13 - Properties of the Varnishes Prepared from the Acetone Segregated Oils.

Oil	Dry to Touch	Dry Hard	Tack After 24 Hours	Colour	Body	Film
1	$2\frac{1}{4}$	Overnight	Very slight	9-10	A	Tough
2	$2\frac{1}{2}$	Overnight	Slight	9-10	A-	Med. Tough
3	2	Overnight	Very slight	9-10	A-	Tough
4	1	5 Hours	Nil	10	D-E	Very Tough
Standard#	$1\frac{1}{2}$	7 Hours	Very slight	11	D	Tough

#-The standard oil in these tests is one of the best commercial, polymerized solvent-extracted oils.

and is recovered from the extractor. Thus, the whole oil is readily segregated into three fractions: (a) An oil for the manufacture of shortening, (b) A low bodied oil which is extracted slowly and is suitable for use as a drying oil in the leather and protective coating industries, and (c) A high bodied acetone-insoluble oil with desirable properties for the paint and varnish industry.

GENERAL DISCUSSION

The primary aim of this investigation was to establish the optimum conditions of heat polymerization and solvent segregation of linseed oil for the production of a "non-reverting", edible shortening and an improved drying oil. The presence of linolenic acid in the edible fraction is most undesirable, whereas it is obviously advantageous to have a high content in the drying oil fraction. Therefore, the process of polymerization is carried out under conditions which permit the highest degree of selectivity in the solvent segregation. The main difference between this process and that now in use in industry is that in the latter high temperatures (300°C and over) are employed to speed up the reactions and increase the rate of production and yield of the polymerized oil. Furthermore, it is not general practice to pass an inert gas through the oil during heating as has been found to be very important in our process. It would appear that our process could be readily adapted to industrial practice.

The nature of the refractive index curve (Figure 5), and the relationship between unsaturation and the refractive indices (Figure 6), indicate that the polymerization reactions take place in a definite sequence. This is most apparent at the lower temperatures. Study of the polymerization

reaction leads to the conclusion that this sequence of reactions is highly selective. The selectivity appears to be related to the level of unsaturation in the triglyceride molecule. Evidence supporting this postulate is to be found in the results of the solvent segregation studies, fractionation of the fatty acids, ultraviolet absorption spectra and chromatographic analyses. Ultraviolet absorption data also indicate that subsequent as well as primary polymerization reactions take place by a diene addition mechanism. This appears to involve the further conjugation of double bonds after the primary polymerization, because the decrease in conjugation does not parallel the increase in the degree of polymerization.

The nature of the reactions are further elucidated by a consideration of the molecular weights of the acetone-insoluble oils and their content of dibasic acids. The data show that the reactions must proceed intramolecularly as well as intermolecularly. The molecular weights of the acetone-insoluble oils also indicate that the predominate structure of the first stage polymers is a dimer and at subsequent stages mixtures of dimers, trimers and perhaps some tetramers. Hence, it appears that a succession of reactions are involved in which the most highly unsaturated triglycerides are polymerized first to form dimers, then trimers, and so on until gelation occurs. Simultaneously,

intramolecular reactions take place to give very complex molecules. This explains the great range of properties of the oils which can be solvent segregated on a basis of the varying complexity of the molecules.

The acetone-soluble oil from which a "non-reverting" shortening can be produced is obviously non-polymeric in nature. The absence of linolenic acid in this fraction is indicated by the fact that the hexabromide test was negative. This would seem to confirm the assumption that linolenic acid is the precursor of the reversion products (1,30). However, all the acids have probably undergone some change in the course of the process. This is indicated by the very pronounced increase in diene conjugation and the presence of solid unsaturated acids. The effect of these changes on the nutrient value of the shortening and the possibility that toxic substance may be present, is being further investigated at the present time. It has also been found that the acetone-soluble fraction of the polymerized oil undergoes enzymatic hydrolysis as readily as natural vegetable oils. The shortenings prepared from this fraction compare favourably with the best commercial brands insofar as the making of pastry is concerned.

It has been shown that the segregation of a non-polymeric oil for the manufacture of shortening and an improved drying oil can be greatly facilitated by a process

involving liquid-liquid extraction. The oil for shortening is readily soluble and can be extracted at low temperatures, thus ensuring a well-defined separation from the polymeric fraction. Since there is a demand for drying oils with varying viscosities, the polymeric fraction can be further segregated to yield the exact type of oil required by industry. The excellent colour, low acid value, quick-drying and range of viscosities of these oils makes them superior to the best commercial, polymerized solvent-extracted oils. Certain of these oils are preferred for the manufacture of paints and varnishes, whereas others meet the requirements of the leather and protective coating industries.

SUMMARY

1. From the physical and chemical analyses of the products of polymerization, the suggestion is advanced that at the lower temperatures of polymerization the reactions proceed in a selective manner according to the level of unsaturation in the triglyceride molecule.

2. The most highly unsaturated triglycerides, followed successively by those of lesser unsaturation, pass through a definite sequence of reactions to form dimers, trimers, tetramers, etc., until finally gelation takes place.

3. The reactions are intramolecular as well as intermolecular and give rise to highly complex molecules.

4. Observations on the mechanism of both the primary and subsequent polymerization reactions of triglyceride molecules agree with the modern theories of polymerization, including Scheiber's isomerization theory (44,45).

5. The optimum conditions have been established for the high temperature polymerization and solvent segregation of linseed oil to produce a "non-reverting", edible shortening. The best oil is obtained by heating at

270-275°C for 12-15 hours, while carbon dioxide is continuously passed through the oil. Under these conditions the polymerized oil has a refractive index of 1.4850-1.4861 at 25°C and yields from 50-60% of an acetone-soluble oil, the yield depending on the method of segregation. The refractive index of this oil is 1.4820-1.4830 at 25°C and the acid value is less than 1%, calculated as oleic acid. Pie crusts containing shortenings made from the acetone-soluble fraction of the oil have been judged to be of good quality. The best shortenings were obtained by hydrogenating to a refractive index of 1.4615-1.4605 (60°C).

6. Although the shortening prepared from the acetone-soluble oils does not revert, it is unpalatable or toxic to rats, although it is readily digested by lipase in-vitro. This problem is being further investigated by the Nutrition and Chemistry Departments of Macdonald College.
7. The polymerized fraction, which is separated from the shortening oil by its insolubility in acetone, can be further selectively segregated with acetone to give oils of widely different properties. Their excellent colour, low acid value, quick-drying and wide range of viscosities makes these oils superior to the best commercial, polymerized, solvent-extracted oils.

CLAIMS TO ORIGINAL RESEARCH

1. Development of a process for the production of a "non-reverting" shortening and an improved drying oil from linseed oil, based on selective polymerization and solvent segregation.

2. Evidence that the polymerization of linseed oil takes place selectively at the lower temperatures (260-280°C) according to the level of unsaturation in the triglyceride molecule.

3. Evidence that the more unsaturated triglycerides are polymerized first, followed by those of lesser unsaturation through a sequence of reaction to form dimers, trimers, tetramers, etc., until finally gelation occurs.

4. Modification of the Twitchell lead salt-alcohol procedure (52) for the isolation of dibasic acids from highly polymerized linseed oil.

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