chromate used for the oxidation determined (31). Another reason, however, is the difficulty of digesting the comparatively large fat samples containing sufficient phosphorus for a reliable determination. This is especially true of most plant extracts which contain a lower phospholipid content than animal extracts. The author has found the use of sulfuric acid impractical and finally devised the perchloric acid procedure described above. Contrary to King (23), a high acidity did not obviate the necessity of controlling pH, nor could this be accomplished by using fixed amounts of acid (perchloric) before digestion. Consistent results were obtained and maximum color developed after 5 minutes by neutralizing the digestion mixture and adding sulfuric acid to a final normality of about 0.5 as described.

Summary and Conclusions

The total extract, phospholipid, unsaponifiable matter, and total fatty acids were determined on 6 samples each of soybean oil meal, cottonseed oil meal, meat and bone scraps, alfalfa leaf meal, wheat ~~gray~~ shorts with screenings, and whole oats and on 5 samples of barley, using both the 16-hour anhydrous ether method and a 3 + 1 alcohol-ether method of extraction. With the exception of whole oats and barley the total ether soluble extract was considerably greater by alcohol-ether extraction than by ether extraction, especially so in the case of soybean meal and cottonseed meal. The non-phospholipid fatty acids, however, showed no significant difference between the two methods of extraction, the differences in total fatty acids being accounted for by the different amounts of phospholipid fatty acids.

The total extract is a poor criterion of the lipid feed value of some feeds, especially alfalfa leaf meal and soybean meal. However, the ethyl ether method more nearly approximates the total fatty acid content than does the alcohol ether method of extraction.

Much of the total extract cannot be accounted for in the sum of the phopholipid, unsaponifiable matter and fatty acid contents as determined.

A method is presented for the determination of phospholipid in plant tissue.

The significance of the lipid analysis of the feeds investigated and the relative values of the anhydrous ether and a 3 + 1 alcohol ether methods of analyses are discussed.

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Studies on the Heat Polymerization and Solvent Segregation of Vegetable Oils[1,2]

O. S. PRIVETT, W. D. McFARLANE, and J. H. GASS

Department of Chemistry, Faculty of Agriculture, McGill University, Macdonald College
Quebec, Canada

THERMAL treatment of vegetable oils is an old and commonly used industrial practice, and the nature of the polymerization reaction has been quite extensively investigated. Since the unsaturated acids alone are involved, most of these studies have been made with monohydric alcohol esters of the unsaturated acids, thus avoiding the formation of highly complex molecules (1, 2, 4, 7, 10, 11). It is generally conceded that the first products of the polymerization contain six-membered hydro-aromatic carbon rings, formed essentially by the mechanism proposed by Kappelmeier (7) and in conformity with Schreiber's isomerization theory (10).

There is not, however, the same unanimity of opinion as to the constitution of the products formed in the polymerization of vegetable oils. Such studies are complicated by the fact that mixed triglycerides undergo intramolecular as well as intermolecular reactions to form complex linear and three dimensional polymers. The elucidation of the constitution of these polymers is rendered difficult by the inherent limitations in the available analytical procedures. Furthermore, the conditions of thermal treatment heretofore employed, promote side reactions and permit the accumulation of decomposition products which are also subject to polymerization.

In a previous communication (9) describing the optimum conditions for the heat polymerization and solvent segregation of linseed oil to produce a "non-reverting" shortening and an improved drying oil we emphasized the importance of the conditions of polymerization in relation to the rate of the reactions

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[2] Presented at the 20th annual fall meeting, American Oil Chemists' Society, Oct. 30-Nov. 1, 1946, in Chicago, Ill.

and the nature of the products obtained. The results suggested that the polymerization was more selective when relatively low temperatures (260-275°C.) were employed and side-reactions were minimized by passing carbon dioxide through the heated oil, thus removing volatile decomposition products as soon as they were formed.

This paper describes further studies on the polymerization of linseed and soybean oils under the same controlled conditions, the objective being to obtain a detailed analysis of the primary polymerization reactions. Certain practical aspects are also considered in a study of the solvent segregation of the polymerized oil and the properties of the various oil separated out.

Methods

I. *Polymerization and Solvent Segregation*

Heat polymerization was carried out by the procedure already described (9) and the temperature was maintained within ±0.5°C. by a mercury immersion thermostat. Solvent segregations were made by a batch process and also by continuous liquid-liquid extraction, employing acetone as the solvent.

Batch separations were made by pouring the polymerized oil into 1,500-1.700 ml. (six volumes) of acetone in a round-bottomed flask, cooling to 5°C. and allowing to stand overnight at this temperature. The supernatant was decanted from the insoluble oil, the acetone distilled off, and the last traces removed from each fraction under reduced pressure.

In continuous liquid-liquid extraction 30 g. of oil were transferred to the extractor, approximately an equal volume of acetone was added, and the mixture was shaken until the acetone was taken up by the oil. Saturating the oil with acetone ensured uniformity and selectivity in extraction and eliminated the tendency for the oil to separate into two layers. The extractions were usually carried out at 20°C., the temperature being maintained by immersing the extraction chamber in a water bath.

II. *Analytical Procedures*

Ultraviolet absorption measurements were made with a Beckman Photoelectric Spectrophotometer. Purified diethyl ether was used as the solvent and the solutions were diluted to give an optical density of 0.2 to 0.8. The results are expressed in terms of the specific absorption coefficient according to the formula:

$$\text{Specific } \alpha = \frac{\log_{10}\frac{I_0}{I}}{c.\,l.}$$

where α = absorption coefficient

I_0 = intensity of radiation transmitted by the solvents

I = intensity of radiation transmitted by the solution

c = conc. of solute in g. per liter

l = depth of solution in centimeters.

Refractive indices were measured at 25°C., using an Abbe refractometer with the prism temperature regulated by water from a Hoppler Ultra-Thermostat. Iodine numbers were determined by the method of Kaufmann as described by Jamieson (6) except that in the analysis of fatty acid fractions a stronger (0.3N) bromine reagent was used. When a reaction time of two hours was used the results agreed closely with those obtained by the Hanus procedure (4A). As with the methods in which glacial acetic acid is used in the reagent, the values varied according to the temperature and time of reaction (1, 11A). However, greater accuracy was obtained with this method on polymerized oils when identical conditions were employed. This method also was used by Bradley and his associates (2, 2A) apparently in preference to the Wijs method. Notwithstanding the fact that substitution may result with stronger bromine solutions, a 0.3N solution was used in the analysis of the fatty acid fractions in an effort to detect the presence of any octadecatrienoic acids.

Solid acids, unsaturated acids, and dibasic acids were determined by the Twitchell lead salt-alcohol fractionation (12) which is based on the fact that the lead salts of the dibasic leads are insoluble in hot acidified 95% ethanol whereas the lead salts of the unsaturated acids and solid acids are soluble and the latter precipitate in a crystalline form on cooling. The molecular weights of the dibasic acid fractions were determined by a modification (8) of the Rast camphor method using sealed capillaries.

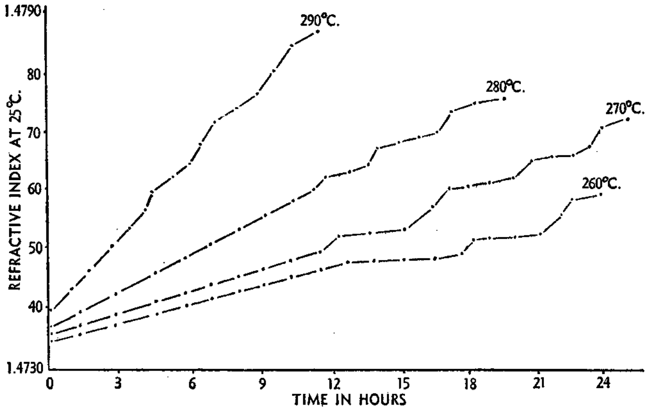


FIG. 1. Showing the relationship between the refractive index and the duration of isothermal polymerization of soybean oil at various temperatures.

Viscosity, color, and drying rate were determined by the methods described by Gardner and Sward (5). Viscosity or "body" was measured with a Gardner-Holt Bubble Viscosimeter and color was measured with a Helliger Comparator using the Gardner Color Standards of 1933. The drying time was estimated by pouring a few cubic centimeters of the sample on to a glass plate which was then placed in a vertical position so as to give a film about six inches long. At periodic intervals the film was lightly touched with the finger at a point about two inches from the top to determine when it changed from a wet to a tacky condition. The film was said to be "dried hard" if no distinct impression was made on it when pressed firmly with the finger tip.

Experimental

I. *Studies on Heat Polymerization*

The heat polymerization of degummed, solvent-extracted soybean oil was carried out under the same conditions as have been described for linseed oil (9) and employing temperatures ranging from 260 to 300°C. for varying periods up to 24 hours. The results obtained in the isothermal polymerization of soybean oil at four different temperatures (260°, 270°, 280°, and 290° C. ±0.5°C.) are illustrated in

Fig. 1 where the change in the refractive index is plotted against time of heating. It will be noted that in the initial stages of the isothermal polymerization of soybean oil a linear relationship exists between the refractive index and the time of heating whereas in the latter stages the reactions proceed in a stepwise manner. These curves closely resemble those previously obtained with linseed oil (9) but cover a lower range of refractive indices. It will be seen that the flat portions of the curves persist for a longer time at the lower temperatures, thus suggesting that the reactions proceed in a more selective manner. Solvent segregation of oils polymerized at the lower temperatures may therefore be expected to yield segregates of more uniform composition and properties.

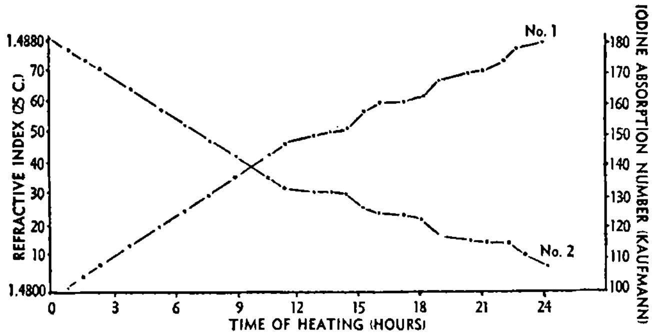


FIG. 2. Showing the relationship between the iodine number, refractive index, and duration of polymerization of linseed oil at 270° C.

No. 1—Refractive Index.
No. 2—Iodine Absorption.

The changes in the iodine number and refractive index during the course of the polymerization of alkali refined linseed oil at 270°C. are illustrated in Fig. 2. Under the conditions employed in this experiment (i.e. the removal of volatile decomposition products, a relatively low temperature of polymerization and determinations of iodine absorption at very frequent intervals), it is revealed that an exact inverse relationship exists between the refractive index and the iodine number—the flat portions in both curves occurring at identical time intervals. This data lends further support to the belief that under these specific conditions the polymerization is of a uniform and selective character and proceeds in a definite sequence of reactions.

In the next experiment samples of alkali-refined linseed oil were polymerized, under the conditions just described, for approximately 13, 17, 21, and 25 hours and designated stages 1-4, respectively. The four oils thus obtained might be considered as representing four stages in polymerization corresponding to the plateaus in the curves in Fig. 2. Each oil was subjected to solvent segregation with acetone, employing the batch method. The fatty acid composition of the acetone-soluble and acetone-insoluble oils was determined with the results given in Table I.

No solid acids were found in the acetone-insoluble polymerized segregates from oils at the initial stages of polymerization, but small amounts were present in the same fractions from oils which had undergone further polymerization. The acetone-soluble oils contained no dibasic acid but had a correspondingly high content of solid acids; the percentage of solid acids increased as polymerization proceeded. These results indicated that the polymerization proceeded according to the level of unsaturation in the triglyceride molecule; the most highly unsaturated being polymerized first, followed by the lesser unsaturated in order of decreasing unsaturation. The Iodine number of the unsaturated acids in this fraction suggested the presence of octadecatrienoic acids. The presence of linolenic acid was highly improbable, and a negative hexabromide test was obtained; however, isomers of this acid may be expected under these conditions of polymerization.

The relationship between the percentage dibasic acids and the molecular weights of the acetone-insoluble polymerized fractions is shown in Table II. The data indicate that intramolecular reactions take place to a considerable degree as the polymerization proceeds.

TABLE II

Analysis of Acetone-Insoluble Fractions From Linseed Oil at Various Stages of Polymerization

Stage of Polymerization	Whole Oil R. Index	Acetone-Insoluble Oils			
		R. Index	Yield of Oil (%)	Yield of 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 molecular weights indicate that in the initial stages of polymerization the polymers are dimers, further polymerization giving rise to a mixture of dimers and trimers. The high molecular weight of the acetone insoluble oil at the last stage of polymerization suggests the presence of tetramers.

The ultraviolet absorption spectra of linseed oil polymerized at 270°C. for varying periods of time up to 24 hours was determined. The spectra showed absorption maxima only at 2320-2340 Å indicating

TABLE I

Results of Fractional Analysis of the Fatty Acids in the Acetone-Soluble and Acetone-Insoluble Fractions From Linseed Oil Polymerized at 270° C. for Varying Periods of Time

Sample	Stage of Polymerization	Solid Acids		Unsaturated Acids			Dibasic Acids		
		Yield*	Iodine Number	R. Index (35°C.)	Yield* (%)	Iodine Number	R. Index (35°C.)	Yield* (%)	Iodine Number
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	43.0	141.0	1.4900	48.0	130.0
	4	Trace	......	1.4704	40.5	139.1	1.4902	54.8	128.2
Alkali-Refined Linseed Oil		8.6	3.5	1.4667	84.3	195.8			

* Yields are expressed as per cent of the original sample and not as per cent of total acids; the theoretical yield of total acids would be about 95%.

diene conjugation. When the specific absorption at 2320-2340 Å is plotted against time of heating at 270°C. (Fig. 3) the rapid increase in diene conjugation in the initial stages of heat polymerization is clearly illustrated. This rapid increase in absorption in the region of 2340 Å has been observed previously by Mitchell and Kraybill (7A) and by Norris et al. (8A) and is in accord with Schrieber's isomerization theory (10).

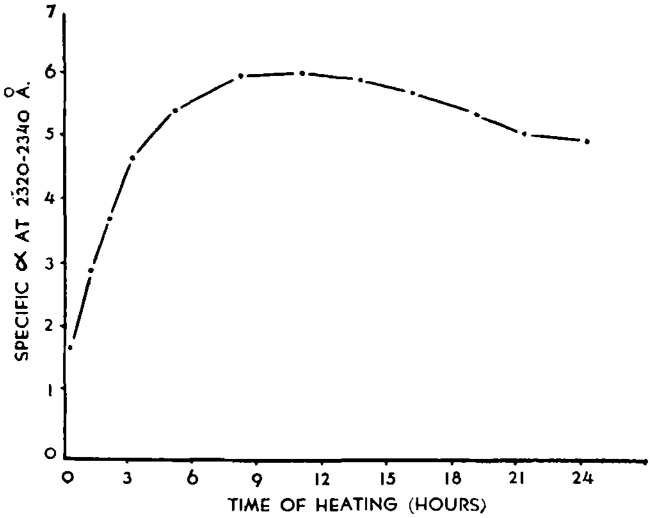


FIG. 3. Showing the relationship between the specific absorption at 2320-2340 Å and the time of heating alkali-refined linseed oil at 270° C.

It will also be noted that diene conjugation reaches a maximum after about 10 hours heating (Fig. 3), which is also the approximate time of heating at which the refractive index curve starts to level-off (Fig. 2). The flattening of the diene conjugation curve from the 10th to the 14th hour indicates the existence of an equilibrium between the rate of conjugation and the rate at which the conjugated isomers are utilized in polymer formation, as suggested by Bradley and Richardson (3). Norris and his associates (8A) also observed this state of equilibrium between diene conjugation and polymer formation on the thermal treatment of the methyl esters of the higher unsaturated fatty acids, and they propose that the decrease in diene conjugation which follows, parallels the increase in polymer formation. However, this does not appear to be the case with the mixed triglycerides. The extent of diene conjugation decreases after about 14 hours' heating but the decrease, amounting to about 20%, appears to be relatively small compared to the increase in polymer formation in the same period; this suggests the reconjugation of some of the double bonds. This is further supported by the data in Table 3 which gives the yield and extent of diene conjugation of a series of fractions from linseed oil polymerized at 270°C. for 17 hours and segregated by continuous liquid-liquid extraction with acetone. The data show that the low-polymer fractions (segregates 7, 8, and 9) are highly conjugated whereas the highly polymerized fractions (segregates No. 12 and 13) are significantly less conjugated. Bradley and Richardson (3) also report only a gradual decrease in the percentage of conjugated acids from the time equilibrium is reached until gelation occurs, which is consistent with the above results.

TABLE III

Refractive Indices and Diene Conjugation of Segregates From Linseed Oil Polymerized at 270° C. for 17 Hours, Obtained by Continuous Liquid-Liquid Extraction With Acetone

Segregate Number	R. Index (25°C.)	Segregation	Diene Conjugation (Specific Absorption at 2320-2340 A)
		Acetone-Soluble Yield (%)	
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

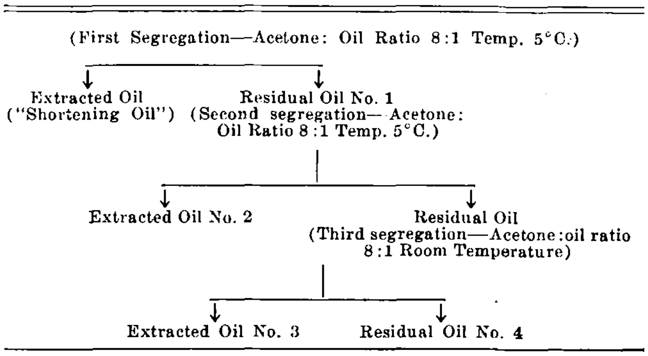
* Insoluble in acetone after 24 hours' extraction.

When considered collectively, the observations recorded above give a general picture of the nature of the polymerization process as it takes place at the lower temperatures and under the described conditions. The polymerization is selective in that it proceeds according to the level of unsaturation in the triglyceride molecule, i.e., the most highly unsaturated are polymerized first, then the lesser unsaturated in order of decreasing unsaturation. Thus a well defined sequence of reactions take place to form dimers, trimers, tetramers, etc., and simultaneously intramolecular reactions give rise to highly complex macro-molecules.

II. *Application to the Preparation of Improved Drying Oils*

The practical significance of polymerizing at low temperatures lies in the fact that the product can be segregated with an immiscible solvent, such as acetone, to give a number of oils of varying constitution and properties. For example, alkali-refined linseed oil was heated for 12½ hours at 270°C. under the conditions described above, and fractionated with acetone according to the following scheme:

POLYMERIZED LINSEED OIL



(First Segregation—Acetone: Oil Ratio 8:1 Temp. 5°C.)

Extracted Oil ("Shortening Oil")

Residual Oil No. 1 (Second segregation—Acetone: Oil Ratio 8:1 Temp. 5°C.)

Extracted Oil No. 2

Residual Oil (Third segregation—Acetone: oil ratio 8:1 Room Temperature)

Extracted Oil No. 3

Residual Oil No. 4

The first and most readily extracted fraction comprising about 50% of the original oil contained no dibasic acids and was therefore non-polymeric in nature. This oil had an acid value of less than 1% calculated as oleic acid and could be hydrogenated to produce a "non-reverting" shortening (9). The residual oil No. 1 segregates on the basis of the complexity of the polymers, the low-polymer fractions No. 2 and No. 3 were extracted into acetone very slowly whereas the most complex molecules were relatively insoluble in acetone, i.e. residual oil No. 4.

TABLE IV

Properties of Drying Oils Segregated With Acetone From the Polymer Fraction of Heat Polymerized Linseed Oil

Fraction Number	The Oils					The Varnishes					
	Color	Body	Drying Time (Hours)		Tolerance Mineral Spirits	Color	Body	Drying Time (Hours)		Film	Tack After 24 Hours
			Without Drier	With Drier				Dry to Touch	Dry Hard		
1	2	W-X	94	7½ Tacky	Very High	9-10	A	2¼	Overnight	Tough	Very Slight
2	2	K-L	94	7½ Tacky	Very High	9-10	A–	2½	Overnight	Med. Tough	Slight
3	2	U	94	Almost Dry	Very High	9-10	A–	2	Overnight	Tough	Very Slight
4	2-3	Z_4-Z_5	94	Almost Dry	Very High	10	D–E	1	5	Very Tough	Nil
Standard	6-7	Z_3-Z_4	86	Almost Dry	Very High	11	D	1½	7	Tough	Very Slight

The properties of the four polymerized segregates as modified drying oils are summarized in Table IV and compared with a commercial sample of heat polymerized solvent extracted linseed oil which was included as a standard. The high-polymer fraction No. 4 was superior in every respect to the standard as a varnish vehicle. The low acid value (less than 1% as oleic acid), excellent color, low viscosity, and quick drying properties of the other polymer fractions, indicates that they would find many preferred uses in the drying oil industries as, for example, in the manufacture of protective coatings.

Four samples, representing four stages in the polymerization of alkali-refined linseed oil at 270°C. and corresponding to the four plateaus in the refractive index curve (Fig. 2) were subjected to continuous liquid-liquid extraction with acetone at 20°C. in a multiple extraction unit under identical conditions. The data obtained in this experiment is presented in Table V.

The trend in the refractive indices in relation to the time of extraction shows that the original oils are composed of three main fractions viz., a readily extracted portion (segregate No. 1), a portion which is extracted slowly and corresponds to a marked increase in refractive index, and a highly insoluble portion which is recovered from the extractor. The first segregate is non-polymeric in nature and as polymerization proceeds from stage I to stage IV the percentage decreases and obviously it is extracted in a shorter time. The second fraction consists of a series of segregates comprising oils which have undergone initial polymerization to varying degrees but are still soluble in acetone. The highly polymerized residual oil has a very high refractive index and viscosity and a high content of dibasic acids; the percentage yield of this fraction increases rapidly as polymerization proceeds.

The segregation of these polymerized oils can be conveniently carried out by continuous liquid-liquid extraction to yield fractions which are similar to those obtained in the multiple batch process. By varying the duration of the thermal treatment, different yields of non-polymeric oil can be obtained and by controlling the continuous extraction process the polymerized fraction can be segregated into a series of oils with different properties.

Summary

The heat polymerization of linseed oil has been studied under specific conditions involving the use of relatively low temperatures (260°-275°C.) and the removal of volatile decomposition products by the continuous passage of carbon dioxide. These conditions minimize side reactions due to decomposition products and permit detailed analyses of the primary polymerization reactions. The results of physical and chemical analyses indicate that polymerization proceeds according to the level of unsaturation in the triglyceride molecules, i.e., the most highly unsaturated are polymerized first, followed by the lesser unsaturated in order of decreasing unsaturation. Thus a well defined sequence of reactions take place to form dimers, trimers, tetramers, etc., and simultaneously intramolecular reactions give rise to highly complex molecules.

The results are of practical significance since they indicate that under the prescribed conditions of heat polymerization a high degree of selectivity can be achieved in solvent segregation to provide a series of oils with a wide range of properties. Thus, segregation with acetone yields a non-polymer fraction suitable for the manufacture of an edible shortening, a low-polymer fraction with the desired properties of a drying oil and a high-polymer fraction particularly suitable as a varnish ingredient.

Acknowledgments

We are specially indebted to the Sherwin-Williams Company of Canada Limited, Montreal, for the determination of the properties of the drying oils.

This investigation was supported by scholarships

TABLE V

Yield and Refractive Index of Segregates Obtained by Continuous Liquid-Liquid Extraction at 20° C., of Samples Representing Four Stages in the Heat Polymerization of Linseed Oil

Segregate Number	Stage I (Approx. 13 Hours at 270°C.)			Stage II (Approx. 17 Hours at 270°C.)			Stage III (Approx. 21 Hours at 270°C.)			Stage IV (Approx. 25 Hours at 270°C.)		
	Extraction Time (Hours)	Yield (%)	R. Index (25°C.)	Extraction Time (Hours)	Yield (%)	R. Index (25°C.)	Extraction Time (Hours)	Yield (%)	R. Index (25°C.)	Extraction Time (Hours)	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	3.5	7.6	24	3.0	9.0	20
4	10.5	3.0	32	7.5	5.5	30	4.5	5.0	32	4.0	8.5	24
5	13.5	5.7	41	9.5	5.9	40	5.5	2.1	39	5.0	5.5	34
6	25.0	5.4	60	11.0	2.0	48	7.0	2.1	48	6.0	2.0	40
7				12.0	4.5	60	9.0	3.8	58	8.0	2.5	48
8				24.0	4.5	90	12.0	5.0	73	10.0	1.5	59
9							24.0	6.3	98	13.0	3.5	70
10										22.5	4.0	92
Residual Oil (Insoluble)	25.0	19.8	1.4930	24.0	24.9	1.4940	24.0	31.6	1.4942	22.5	43.2	1.4942

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Vapor Phase Dehydrochlorination of Chlorinated Fatty Substances

II. Catalytic Process Applied to Various Chlorinated Fatty Materials[*]

G. R. VAN ATTA, D. F. HOUSTON and W. C. DIETRICH

Western Regional Research Laboratory,[1] Albany, California

Introduction

THE first paper in this series (1) described a method for catalytically dehydrochlorinating chlorinated fatty acids in the vapor phase at low pressures. Therein were presented results of experiments conducted with the mixture of acids that is obtained when palmitic acid is treated with chlorine gas until an average of about two equivalents of chlorine are combined per mole of acid.

The present paper reports work done on a limited number of other chlorinated fatty materials. Further experiments comparing the behavior of chlorinated palmitic acid containing differing amounts of chlorine and prepared in different ways are also reviewed. A brief discussion is included of the possible utility and the limitations of the vapor-phase process as they now appear.

Chlorinated Materials

Chlorinated methyl palmitate was prepared from purified methyl palmitate by direct chlorination at 40-59° C. Before chlorination the ester had an iodine value of less than 0.5 and its saponification equivalent was 270.7; theoretical for methyl palmitate, 270.44. The chlorinated product contained 21.6% of chlorine; theoretical for methyl dichloropalmitate, 20.9%.

Three lots of chlorinated palmitic acid were used. Two lots, those used in Experiments 21 and 44 (See Tables I and II, and following text) were prepared from purified palmitic acid by the method described in the previous paper. The chlorinated acid used in Experiment 21 contained 36.8% of chlorine and that used in Experiment 44 contained 22.1% of chlorine. The chlorine contents of tetrachloro- and di-chloropalmitic acids are 35.98% and 21.80%, respectively.

The third lot of chlorinated palmitic acid, which was used in Experiment 49, was prepared by saponification of the chlorinated methyl ester previously described. During saponification and recovery some of the chlorine was hydrolyzed with the result that the free acid contained 18.1% of chlorine and had an iodine value of 2.2.

Chlorinated stearic acid containing 20.3% of chlorine was prepared by direct chlorination of stearic acid previously purified by fractional crystallization from solvents. The purified stearic acid melted at 68.2 to 69.3° C. and its neutral equivalent was 285.0. Dichlorostearic acid contains 20.07% of chlorine.

Chlorinated oleic acid was prepared from purified oleic acid obtained from olive oil. The oleic acid had an iodine value of 89.6 and its neutral equivalent was 283.6; theoretical values for pure oleic acid, 89.9 and 282.46, respectively. In chlorinating this acid, conditions were chosen which were intended to favor addition of halogen to double bonds and allow a minimum of substitution. Chlorination was effected by slowly pouring a 0.9 *N* solution of chlorine in methylene chloride cooled to —20° C. into a 10% solution of the acid in the same solvent at the same temperature. The temperature of the mixture was not allowed to rise above —8° C. during the addition. The quantity of chlorine added was limited to 95% of the amount required for saturation of the oleic acid. Five minutes after mixing, the solution was put under reduced pressure, and a stream of nitrogen was bubbled through it to assist in removing any unreacted chlorine. After the solution was purged of free chlorine, the solvent was removed by distillation at reduced pressure. The chlorinated product contained 18.0% chlorine and had an iodine value of 9.6. Calculations based on these figures and the iodine value of the original acid indicate little if any chlorination occurred by substitution. Assuming that no substitution did occur, the chlorinated product was comprised

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.