

It is not known however whether polymers are formed in unsaturated triglycerides during the initial stages of autoxidation. Whether polymers are formed during the initial stages or only after prolonged autoxidation seems irrelevant to their function as precursors of reversion components. If formed during the initial stages, they are present in the oil *per se*. If formed only after prolonged autoxidation, the polymers could be preformed and dissolved in fresh soybean oil. For example, the polymeric substance found on the filter press could have been formed from oil previously passed through it. The polymers could then be dissolved by fresh oil as it passes through the contaminated press. However this does not mean that the filter press is the only place where oxidative polymers could be formed and contaminate soybean oil. For example, the deodorizer is another point where oxidative polymers might be formed. If inward leakage is not completely prevented or if the steam is not entirely free of air, the oil in the deodorizer, during the several hours of heating at relatively high temperature with vigorous agitation, may form small amounts of polymers. It is therefore possible that whenever the conditions are suitable, soybean oil could form oxidative polymers. Any odorous compounds formed during polymerization may be subsequently removed by deodorization, but the polymers may remain in the oil and serve as a precursor of reversion compounds.

Golumbic and Daubert (12) pointed out that only a very small amount of oxygen is required to produce reversion. Furthermore Robinson and Black (13) observed flavor deterioration in soybean oil aged under inert gases, and Bickford (14) reported that reversion could occur during storage under high vacuum. All these observations can be explained with the present data. These data showed that the oxidative polymers are 9.24% higher in oxygen content than fresh refined soybean oil and could decompose without further absorption of much more oxygen. Since the oxidative polymers were shown to decompose under high vacuum or nitrogen, the excluding of air could only prevent autoxidation of the unsaturated triglycerides but not the decomposition of the more polar polymers with the resulting formation of volatile carbonyl compounds. It is therefore evident that soybean oil containing small amounts of oxidative polymers could revert when aged under these conditions.

### Summary

The polymers formed during the autoxidation of soybean oil at 60°C. were isolated by a solvent-extraction method, using diethyl ether and pentane-hexane as solvents. The more polar polymer fraction was further oxidized by air at 30°C., and the volatile material obtained was fractionated and characterized. It contained the same carbonyl compounds as the volatile material which has previously been obtained from reverted soybean oil, namely acetaldehyde, propionaldehyde, n-hexanal, and 2-pentenal.

The more polar polymer fraction contained 21.04% of oxygen and degraded to volatile carbonyl compounds under vacuum as well as under oxygen-free nitrogen. Depolymerization and ethanolysis of these polymers were carried out in ethyl alcohol which had been adjusted to a normality of 3.5 with anhydrous hydrogen chloride. The polymeric substance formed on the filter presses of a soybean oil refinery could be depolymerized in a similar manner. It is therefore evident that oxidative polymers could be unintentionally introduced into soybean oil in various ways and serve as precursors of reversion compounds.

### Acknowledgment

The authors wish to acknowledge Ruby Chen for molecular weight determinations, Ralph Fessenden for Lappin Clark tests and peroxide number determinations, and Alberta Schmidt for chromatographic separations of the 2,4-dinitrophenylhydrazones.

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[Received December 23, 1953]

## Dilution Polymerization of Linseed Oil<sup>1, 2</sup>

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IN thermal polymerization of fats and oils, reactions may occur between acyl groups within the same glyceride molecule or between acyl groups of different molecules. The first possibility results in a loss in unsaturation but does not increase molecular weight. Its popular name, "intra-polymerization," is therefore misleading. The second reaction, "inter-polymerization," is a genuine polymerization in that molecular enlargement results.

Because the importance of intra-glyceride reactions is still a matter of controversy, an investigation of this reaction was undertaken. Polymerization in the presence of a diluent was used on the assumption that reaction between acyl groups within the same triglyceride molecule is of lower kinetic order than reaction between triglycerides.

### Materials and Methods

In this study, linseed oil was polymerized, and "heavy" white mineral oil was used as diluent.

<sup>1</sup>N.R.C. No. 3322.

<sup>2</sup>Part of this paper was presented at the Protective Coatings Section, Chemical Institute of Canada, Montreal, June, 1952.

TABLE I  
 Polymer Formation at 280°C.

Heating time, hr.	100% Linseed Oil			20% Linseed Oil			10% Linseed Oil		
	Polymeric Glycerides %	Polymeric Acyl Groups %	Ratio of Acyl Groups Glycerides	Polymeric Glycerides %	Polymeric Acyl Groups %	Ratio of Acyl Groups Glycerides	Polymeric Glycerides %	Polymeric Acyl Groups %	Ratio of Acyl Groups Glycerides
0	1.3	1.7	1.32	0.6	1.2	1.33	0.2	0.9	4.5
1	7.0	3.4	0.49	1.5	1.6	1.10	0.5	1.4	2.8
3	19.4	10.1	0.52	5.0	2.6	0.52	0.0	2.7	....
5	26.9	14.3	0.53	9.8	5.0	0.51	0.2	3.8	19.0
6	30.1	16.1	0.53	10.4	5.2	0.52	0.4	4.9	12.2

The vegetable oil was alkali-refined and bleached at 110°C. with 2% Superfiltrol. The mineral oil was molecularly distilled to remove the more volatile components.

The oils were polymerized by heating in an all-glass reaction vessel immersed in a wax bath, kept within  $\pm 0.5^\circ\text{C}$ . by an Aminco high temperature bimetallic regulator. Temperatures were measured by an iron-constantan thermocouple located in a well in the reaction vessel. This thermocouple, and its recording potentiometer, had been calibrated against a platinum resistance thermometer.

In experiments with linseed oil, at 280°C. and 290°C., the oil and diluent were mixed in the reaction vessel before immersion in the thermostat. The reaction mixture was heated for approximately 18 min., the time required for the system to reach reaction temperature, before the initial sample was taken. In later work, involving 20% linseed oil at 270°C. and 280°C., the mineral oil diluent was weighed directly into the reaction vessel; and when it reached reaction temperature, a known weight of triglyceride was added rapidly. When this technique was used, 10% added glyceride required 2 min. to reach temperature and 20% added glyceride, 4 min. Purified nitrogen was used to agitate the reaction mixture and to sweep out volatile products.

The samples were collected in an evacuated receiver and cooled under nitrogen. A portion of each sample was analyzed for polymeric triglyceride, using a micro-molecular still (3). Another portion was saponified to separate the fatty material from the diluent. The soaps were decomposed and the fatty acids were converted to methyl esters with diazomethane to obviate the heating that ordinary esterification procedures require. Until the ease with which polymeric esters are adsorbed on drying agents was recognized, low values for polymeric esters were obtained. However washing the drying agent with several portions of undried ether released the ester. The ether was removed at 35°C. under vacuum.

Specific refraction was calculated from refractive index measured with a Bausch and Lomb Precision Refractometer to  $\pm 0.00003$ , and from density determined to  $\pm 0.0002$  by the falling drop method (4). Molecular weights were estimated from a graph of molecular weight *versus* refractive index, using the Signer method with n-butane and extrapolating to zero concentration. Oil from the same batch was used in the molecular weight determinations and in the polymerization studies.

Dienoic and trienoic acyl groups were determined spectrophotometrically by the A.O.C.S. standard method. For isomerization periods of 6 hours, percentage of diene and triene was computed, using Paschke's (2) value of 86.6 for the specific extinction coefficient of diene and a value of 33.3 for triene,

obtained by isomerizing methyl linolenate for periods of 0.42, 1.5, 3.0, 4.5, and 6.0 hours. The empirical constants in the percentage calculation were correspondingly modified.

Infrared spectra were determined in carbon tetrachloride solution, using a rock salt prism, a 0.5-mm. cell, and concentrations of 2% by weight.

## Results

*Polymer Formation.* The amount of inter-glyceride reaction was reduced by the presence of diluent (Table I). Conditions that produced inter-polymer in the absence of diluent failed to produce polymeric triglycerides in 90% diluent and produced reduced amounts in 80% diluent. Conversion of the heat-treated triglyceride oils to simple esters and distillation to remove monomeric from dimeric esters showed (Table I), that, with linseed oil, polymeric acyl groups had been formed in the absence of inter-glyceride reaction.

Both the method of preparation of the esters and their molecular distillation were tested to see if they produced polymeric material. A sample of methyl linolenate, saponified, re-esterified, and distilled in the regular manner, failed to show any polymeric material. Therefore the methods used in this investigation were considered adequate under ordinary circumstances. Occasionally, however, the 0-hr. sample contained polymer. Part of this material could have been formed during the time required for the oil to reach reaction temperature. Part was probably due to peroxidation after sampling. The peroxides, thus formed, catalyzed polymerization in the still. The influence of peroxides on thermal polymerization has been reported elsewhere (5, 9).

The ratio of polymeric acyl groups to polymeric triglyceride groups was approximately 0.5 when the

 TABLE II  
 Polymer Formation at 270, 280, 290°C.

Heating time, hr.	100% Linseed Oil, 270°C.			10% Linseed Oil, 270°C.		
	Polymeric Glycerides, %	Polymeric Acyl Groups, %	Ratio of Acyl Groups Glycerides	Polymeric Glycerides, %	Polymeric Acyl Groups, %	Ratio of Acyl Groups Glycerides
0.05	0.60	1.20	2.00	1.28	1.10	0.86
1.0	4.42	1.41	0.32	1.18	1.74	1.47
2.0	6.12	2.15	0.35	1.38	2.10	1.52
3.0	9.26	4.09	0.44	1.00	3.51	3.51
5.0	14.42	6.64	0.46	1.68	4.25	2.53
7.0	20.82	10.00	0.49	4.28	4.60	1.07
10% Linseed Oil, * 280°C.						
0.05	0.00	0.00	.....	0.50	0.50	1.00
1.0	1.20	1.20	1.00	1.10	0.71	0.65
2.0	2.60	2.40	0.92	.....	.....	.....
3.0	4.02	3.48	0.86	3.20	2.00	0.62
5.0	5.62	5.60	1.00	7.70	5.20	0.67
7.0	7.85	7.50	0.94	.....	.....	.....
10% Linseed Oil, 290°C.						
0.05	0.00	0.00	.....	0.50	0.50	1.00
1.0	1.20	1.20	1.00	1.10	0.71	0.65
2.0	2.60	2.40	0.92	.....	.....	.....
3.0	4.02	3.48	0.86	3.20	2.00	0.62
5.0	5.62	5.60	1.00	7.70	5.20	0.67
7.0	7.85	7.50	0.94	.....	.....	.....

\* Peroxidized oil, P.V. = 45.

diluent was present in concentrations of less than 80% and greater than unity at 90% diluent (Table I). Two additional factors that might affect the size of the ratio are temperature and peroxide content of the oil. Polymerization at 270°C. and 290°C. with normal oil and at 280°C. with peroxidized oil showed (Table II) that increasing polymerization temperature and peroxide content reduced the ratio of polymeric acyl groups to polymeric triglyceride groups.

**Disappearance of Unsaturation.** The following information was obtained from spectrophotometric analysis of samples of oil heated in the absence of diluent (Table III). Formation of conjugated diene was the same as that described by other workers, *i.e.*, conjugation increased slowly to a maximum and then fell off slowly. At no time could a positive specific extinction coefficient for conjugated triene be calculated. The concentrations of unconjugated diene and triene diminished with the time of heating in an apparently first order manner.

TABLE III

Changes in Unsaturation of Linseed Oil Heated in the Absence and Presence of Diluent

Functional group	Heating time, hr.	100% Linseed Oil		10% Linseed Oil			
		S.E.C. <sup>a</sup>	% <sup>b</sup>	280°C.		290°C.	
				S.E.C. <sup>a</sup>	% <sup>b</sup>	S.E.C. <sup>a</sup>	% <sup>b</sup>
Conjugated Diene 233 m $\mu$	0	1.87	0.74	1.26	0.21	1.62	0.52
	1	4.89	3.37	2.25	1.07	2.87	1.61
	3	5.89	4.24	3.01	1.73	3.48	2.14
	5	6.53	4.79	3.46	2.12	3.54	2.19
	6	5.70	4.07	....	....	....	....
	Conjugated Triene 268 m $\mu$	0-6	....	Nil	....	Nil	....
Unconjugated Diene 233 m $\mu$	0	44.06	16.44	39.52	11.17	35.27	6.48
	1	40.53	12.77	41.56	12.39	36.03	8.10
	3	38.11	12.07	39.25	13.04	31.36	10.57
	5	35.39	11.84	35.80	8.34	26.26	5.79
	6	31.02	9.58	....	....	....	....
	Unconjugated Triene 268 m $\mu$	0	5.96	45.95	5.98	46.00	5.97
1		5.24	40.38	6.09	46.94	5.57	42.94
3		4.64	35.76	5.50	42.39	4.36	33.60
5		4.06	31.30	5.35	41.25	3.77	29.06
6		3.63	27.97	1.51	11.64	....	....

<sup>a</sup>S.E.C. = specific extinction coefficient for wave lengths shown in first column.

<sup>b</sup>Calculated by A.O.C.S. "long" method.

With dilution polymerization of linseed oil at 280°C., formation of conjugated diene was the same as in the absence of diluent, and again no conjugated triene was detected (Table III). The concentration of unconjugated diene reached a maximum at 3-hr. heating time and then diminished. However unconjugated triene behaved as in the absence of diluent, disappearing in an apparently first order manner. Like behavior was observed at 290°C.

The apparently anomalous behavior of the unconjugated dienoic material in the samples of oil polymerized in the presence of diluent was reinvestigated, using a 6-hr. period of alkali isomerization. As anticipated, the longer isomerization time produced in each sample an apparent increase in diene conjugation and a decrease in triene conjugation. As a function of polymerization time, non-conjugated triene was shown to decrease and non-conjugated diene to increase.

**Change in Molar Refractivity.** To estimate the extent of molecular change caused by heating, molar refractivities were calculated for samples of oils polymerized in the absence and presence of diluent. Because the diluent was present when density and

refractive index were measured, the changes in these properties of the mineral oil that might occur when it was heated under polymerization conditions were determined. The data indicated that loss in weight was negligible and that the changes in density and refractive index were too small to make a significant difference in the specific refraction.

From the data (Table IV), specific refractions were calculated and plotted as functions of molecular weight (Fig. 1). The lines obtained suggest that the

TABLE IV  
Change in Properties of Linseed Oil Heated at 280°C.

Conditions	Heating time, hours	$d_4^{25}$	$n_D^{25}$	Molecular weight
100% Linseed oil at 280°C.	0	0.9318	1.47873	880
	1.0	0.9329	1.47930	922
	3.0	0.9354	1.48024	1003
	5.0	0.9378	1.48140	1104
	6.0	0.9389	1.48170	1132
	7.0	0.9401	1.48220	1178
	12.0	0.9465	1.48462	1396
20% Linseed oil at 280°C.	15.0	0.9494	1.48543	1452
	0.07	0.8909	1.47883	880
	1.0	0.8914	1.47903	890
	3.0	0.8923	1.47910	898
	5.0	0.8927	1.47919	904
	7.0	0.8929	1.47924	910
	9.0	0.8937	1.47929	914
10% Linseed oil at 280°C. Peroxidized	0.05	0.8826	1.47873	880
	1.0	0.8833	1.47873	880
	3.0	0.8837	1.47873	880
	5.0	0.8840	1.47876	883
	7.0	0.8842	1.47881	887
	9.0	0.8845	1.47888	890
	11.0	0.8847	1.47898	897

change in specific refraction with molecular weight was regular and not discontinuous even when extended to 15-hr. heating time and that the process causing the change was favored by dilution. Like results were also obtained with linseed oil heated at 270°C.

### Discussion

**Effect of Diluent on Thermal Polymerization.** It was assumed, at the start of this investigation, that reaction between glycerides was of higher kinetic

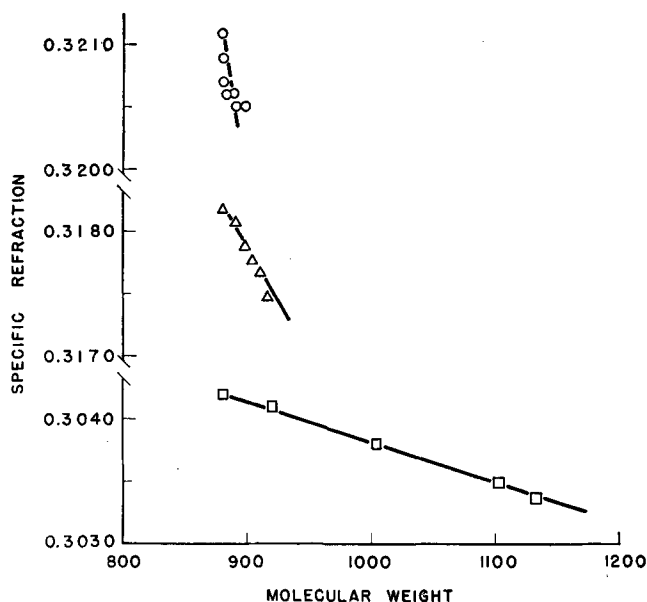


FIG. 1. Specific refraction as a function of molecular weight unperoxidized linseed oil heated at 280°C.

○ 10% oil; △ 20% oil; □ 100% oil.

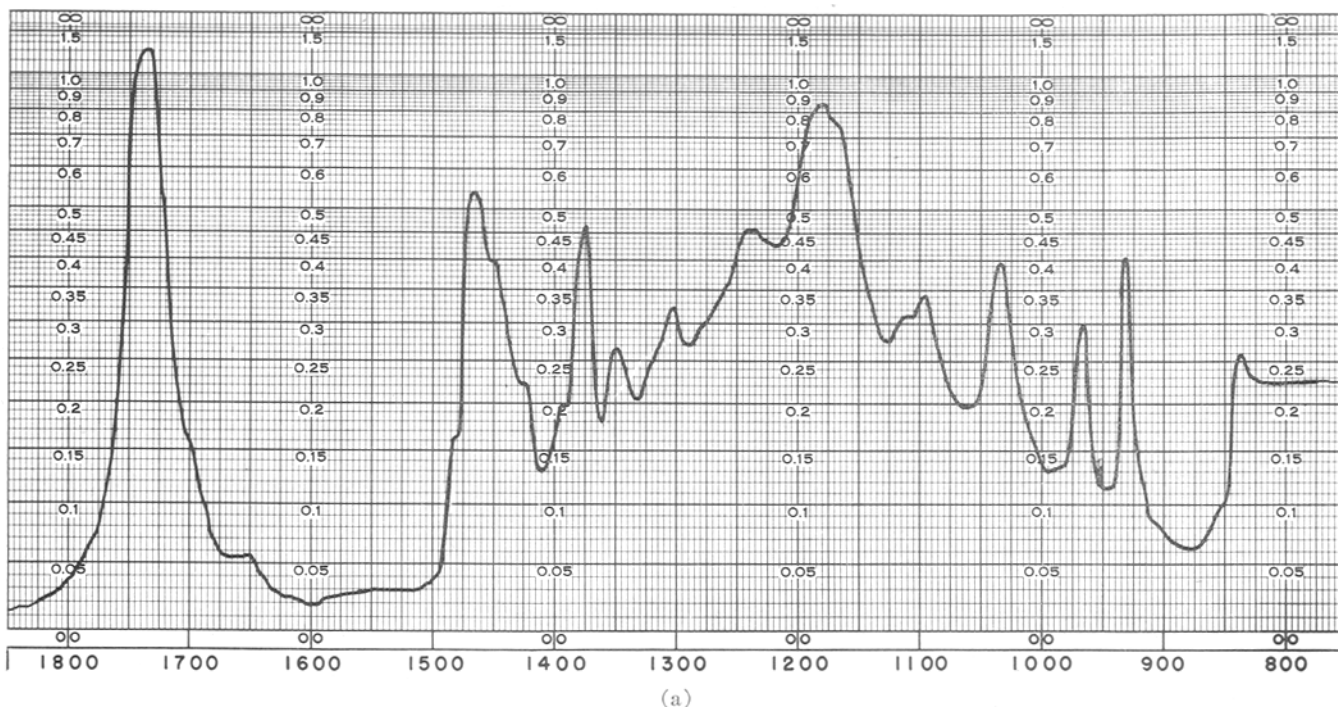


Fig. 2. Infrared spectra of linseed oil methyl esters.

- a) From unheated oil.  
 b) From heated oil, 20% oil at 280°C. for 6 hr.

order than intra-glyceride reaction. However estimation of the kinetic order of these reactions is not simple. Nevertheless, if it can be assumed that the environment of a glyceride molecule is not changed drastically by the presence of mineral oil diluent, certain comments on the order of the reaction are possible. Evaluation of the data for linseed oil at 280°C. by the fractional-life period method resulted in a kinetic order of a range from 1.83 to 1.96 for both the polymerization of glycerides and the sum of inter- and intra-glyceride reactions of acyl groups. Therefore, on the assumption that the rate expression is of the form  $dx/dt = (a - x)^n$ , a reaction order greater than unity and approaching 2 can be offered for thermal polymerization at this temperature. The observed sharp reduction in inter-glyceride reaction with decreasing glyceride concentration can be explained on this basis.

Another consequence of the presence of diluent was an apparent anomaly in the concentration of non-conjugated dienoic material in the heated samples. The behavior was changed by increasing the isomerization time from 25 min. to 6 hr. However, in the absence of information on the rate of alkali conjugation of all the various possible geometric isomers of linolenic acid, a quantitative evaluation of the data is impossible.

If estimation of relative amounts of *trans* unsaturation from optical densities of solutions of like concentration is legitimate, it can be deduced from the infrared spectra (Fig. 2) that all samples of heated oils except the 0-hr. samples, contained *trans* double bonds. Since samples of oil polymerized in the absence of diluent behaved in a conventional manner when isomerized, it is possible that the dilution polymerized samples contained some material that resisted conjugation. Because the saponification

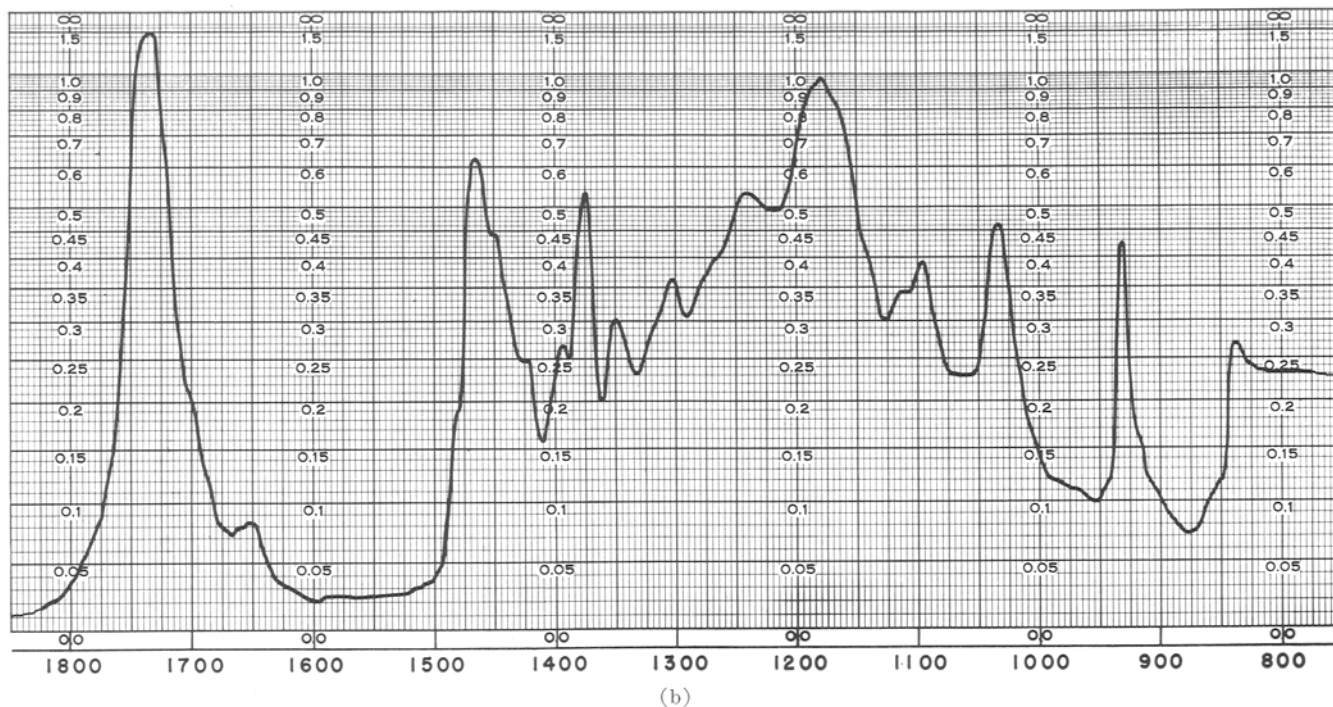
equivalent of a typical ester prepared from dilution polymerized oil was within experimental error of the calculated value, this material could not have been the mineral oil diluent carried over in the preparation of the esters.

*Estimation of Extent of Molecular Change.* Wiseblatt *et al.* (8) considered the two possible intra-glyceride reactions: Type 1, union of two acyl groups in the same monomeric glyceride molecule; and Type 2, union of acyl groups in a polymeric glyceride molecule. A case not discussed by these workers is that of Type 2 intra-glyceride reaction, occurring through union of two acyl groups within a single glyceride unit of the polymer to form a trimeric acyl group. The ratio of percentage by weight polymeric acyl groups to percentage by weight polymeric glyceride molecules has been calculated for a few of the possible systems:

System	Ratio
Inter-polymer only.....	0.33
2/3 inter-polymer: 1/3 Type 2 within one unit.....	0.39
2/3 inter-polymer: 1/3 Type 2 between units .....	0.44
1/3 inter-polymer: 1/3 Type 2 within units: 1/3 Type 2 between units .....	0.50
Inter-polymerization followed by Type 2 within units.....	0.50
Inter-polymerization followed by Type 2 between units....	0.67

The inclusion of trimeric acyl groups is based on results to be published shortly.

The values of the ratio of polymeric acyl groups to polymeric glycerides for linseed oil polymerized at 280°C. in the absence of diluent are larger than 0.33, the value calculated for polymerization unaccompanied by intra-glyceride reaction. However the values of the ratio for 100% linseed at 270°C. start at 0.33 and then grow larger, suggesting initial freedom from



(b)

intra-glyceride reaction. When linseed oil was polymerized in 20% concentration, the values of the ratio were practically unaffected by the presence of diluent. However the much higher values obtained with 90% diluent suggest that intra-glyceride reaction, in the absence of diluent, is not extensive.

Waterman's method of ring analysis (6) has been used to estimate the mean number of rings per molecule of heated ester (7). Since the additivity of atomic refractions is not greater than 1%, the method is inapplicable to compounds of molecular weight greater than 300. Therefore estimation of the number of rings per molecule of glyceride has not been attempted. However the slope of the lines (Fig. 4) represents specific refraction per molecule. Since higher values were obtained at higher concentrations of diluent and the change in slope on increasing the glyceride concentration from 10% to 20% was greater than that effected by going from 20% to 100% glyceride, the reaction mainly responsible for the change in specific refraction can be considered concentration-dependent.

In general, the data presented in this paper suggest that the processes by which unsaturated linkages are consumed, acyl groups and glycerides polymerize, and molecular volumes change, are not simple. A definite dependence of these reactions on concentration has been detected. Although molecular changes, which might indicate ring formation, do occur in dilute solution, their occurrence has not been demonstrated in the absence of diluent. Moreover Boelhouwer *et al.* (1) have shown that the intra-glyceride reaction is not predominant in the early stages of polymerization. The amount of polymeric acyl groups

in monomeric glycerides actually increases during the period of slight iodine value decrease and major viscosity increase.

#### Summary

An inert diluent, molecularly distilled mineral oil, when present in 90% concentration, permitted, in linseed oil, the polymerization of acyl groups in the absence of inter-glyceride reaction. Comparison of the data for the polymerization of linseed oil in 10, 20, and 100% concentrations showed a marked concentration dependence for the following: polymerization of acyl groups and glyceride molecules; change in specific refraction and the ratio of percentages by weight polymeric acyl groups to polymeric glyceride molecules.

#### Acknowledgment

The capable assistance of F. P. Cooper is gratefully acknowledged. The author is also indebted to F. P. Lossing for analysis of nitrogen samples by mass spectrometer and to C. E. Hubley and R. N. Jones for infra-red spectra.

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[Received September 28, 1953]