FIG. 7. Relationship between the extent of the autoxidation of methyl linoleate at 50°C. and A, k₂₃₄ of the products of the autoxidation of methyl linoleate; B, rate of oxidation of methyl linoleate; C, percentage oxidation of accumulated hydroperoxides; D, rate of oxidation of accumulated hydroperoxides.

Summary

1. Kinetic studies showed that concurrent oxidation of preformed hydroperoxides may be expected to take place at all stages of the autoxidation of methyl linoleate. The rate of oxidation relative to the rate of autoxidation of unoxidized ester is determined chiefly by the extent of the accumulation of hydroperoxides.

2. Infrared spectral analysis of hydroperoxides oxidized to various degrees indicated that trans, trans diene conjugation and isolated trans double bonds produced in the autoxidation of methyl linoleate are related to the concurrent oxidation of the accumulated hydroperoxides.

3. The low absorptivity observed for diene conjugation, compared to that which may be expected for the exclusive production of cis, trans diene conjugated hydroperoxide isomers during the autoxidation of methyl linoleate is attributed to the concurrent oxidation of accumulated hydroperoxides.

4. The effect of antioxidants in giving a well-defined induction period in the oxidation of hydroperoxides isolated from autoxidized methyl linoleate

indicated that the oxidation proceeds by a chain reaction.

5. The primary reaction products of the oxidation of hydroperoxides isolated from autoxidized methyl linoleate were found to be polymers formed in a sequence of reaction involving the diene conjugation.

6. Studies on the autoxidation of methyl cis-9, trans-11-linoleate showed that cis, trans isomerization of the conjugated diene took place with the concurrent production of isolated trans double bonds and loss of diene conjugation.

Acknowledgment

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Viscometric Properties of Higher Fatty Acids and Their Derivatives[1]

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VISCOSITY is the internal friction or resistance to flow displayed by a liquid. One of the most important properties of liquids, it is determined by the size and shape of the molecules of the liquid and by the nature and magnitude of intermolecular forces in the liquid. These factors are, in turn, uniquely determined by the chemical and physical structure of the molecules of the liquid, i.e., chain length, the presence or absence of side chains, the nature of polar

groups in the molecule, the existence of hydrogen bonding, and the tendency of the molecules to be linear or coiled, rigid or flexible.

The absolute viscosity of a liquid (expressed as poises) can be calculated from the volume of liquid per unit time that flows under a given pressure differential through a capillary tube of radius r and length l. The equation connecting these variables, known as Poiseuille's Law, is

$$\frac{v}{t} = \frac{\Delta p \pi r^4}{8 \eta l} \qquad (1)$$

where η is the viscosity coefficient. Kinematic viscosity (expressed as stokes) is the ratio of viscosity to density, η/d. It is convenient in the laboratory to determine the length of time required for a known volume of liquid to flow from a capillary pipette calibrated in terms of a standard of known viscosity. The viscosity (η_2) of the liquid is then given by

$$\eta_2 = \eta_1 \frac{d_2 t_2}{d_1 t_1} \qquad (2)$$

where t_1 is the efflux time for the standard liquid of viscosity η_1 and density d_1 and t_2 and d_2 are the efflux time and density of the liquid in question. In practice many precautions must be observed, and corrections must be applied to obtain accurate results.

Because viscosity is determined by molecular structure, efforts have been made to formulate a general kinetic theory of liquids on the basis of which viscosity and its temperature and pressure coefficients would be expressed as functions of variables, such as fields of intermolecular force and rotational degrees of freedom of the molecules in the liquid (14, 18). One of the more interesting results of these theories is that viscosity can frequently be expressed by an equation of the form

$$\eta = Ae^{E/RT} \qquad (3)$$

This equation is identical in form to that governing rate of chemical reaction. For chemical reactions the constant E is interpreted as the heat of activation of the reactants into the intermediate complex. For viscosity the constant is regarded as comprising two terms: one, the heat of activation of formation of holes in the liquid; and two, the heat of activation of motion of other molecules through these holes.

This very brief discussion of the theoretical aspects of viscosity will, it is hoped, give the reader some idea of the background against which the viscometric properties of higher fatty acids and their derivatives must be considered.

Importance of Viscometry of Fatty Acids and Derivatives

In the field of fats and oils viscosity has both theoretical and practical significance. The study of the viscosities of the various fatty acids and their derivatives is important not only because of the relationship between structure and viscosity but also because these relationships can be used to follow the progress of such chemical reactions as polymerization or oxidation. The viscosity of a fatty acid or derivative may be a determining factor in the performance of a product, such as a varnish or lubricant, of which the fatty acid or derivative is an ingredient.

Fatty acids and derivatives can exert a profound effect upon the viscometric properties of other substances. Applications of this effect are the use of soaps in greases, and the use of various fatty acid derivatives as lubricant additives to improve boundary lubrication, lower pour-points, and improve the viscosity index of lubricants. Although not, in general, dependent upon the viscosities of the fatty acid or derivative, these effects are of great importance and may appropriately be considered in connection with a general discussion of the viscometric properties of fatty acids and their derivatives. Owing to the extensive literature devoted to the subject of greases, the present paper will be confined to consideration of

certain other aspects of the viscometry of fatty acids and derivatives.

Viscosity and Structure of Fatty Acids and Their Derivatives

Homologous Series. Viscosities for higher members of several homologous series of fatty acids and their derivatives are shown in Figure 1. Owing to limited
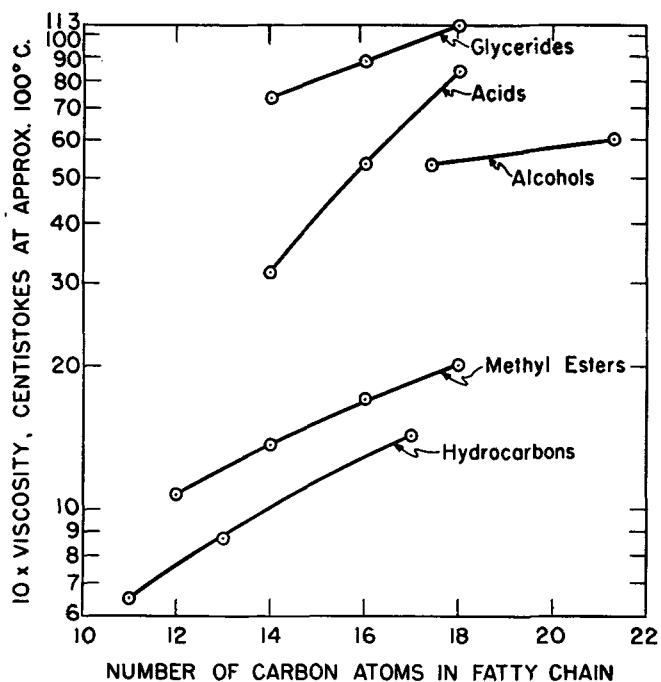

FIG. 1. Viscosities of higher members of homologous series of fatty acids and derivatives. [Data are assembled from the following sources: hydrocarbons, Ref. 13; methyl esters, Ref. 4; acids, extrapolated from data in Ref. 25; alcohols, calculated for mixed alcohols from data supplied by a commercial manufacturer (number of carbon atoms equals the calculated average chain length); glycerides, extrapolated from data in Ref. 22.]

data available, the range of chain lengths included is necessarily restricted. These curves show that the nonpolar hydrocarbons have the lowest viscosities for a given chain length. Polar groups produce increases in viscosity. Glycerides have the highest viscosities, as would be expected on the basis of their molecular weight.

Gros and Feuge (21) have reported viscosities at 75°C. for the homologous series of saturated, even-numbered, n-fatty acids from C_2 to C_{18} and their methyl and ethyl esters. As shown in Figure 2, the free fatty acids have the highest viscosities, and the change in viscosity with increasing chain length is greatest for these acids. The viscosities of the ethyl esters are only slightly greater than those of the methyl esters. This difference is maintained nearly uniformly over the range of chain lengths studied.

Bonhorst, Althouse, and Triebold have reported (4) viscosities at several temperatures in the range of 20° to 100° for methyl, n-propyl, and isopropyl esters of fatty acids from C_6 to C_{18}. Data obtained for these esters at 60° are presented in Figure 3.

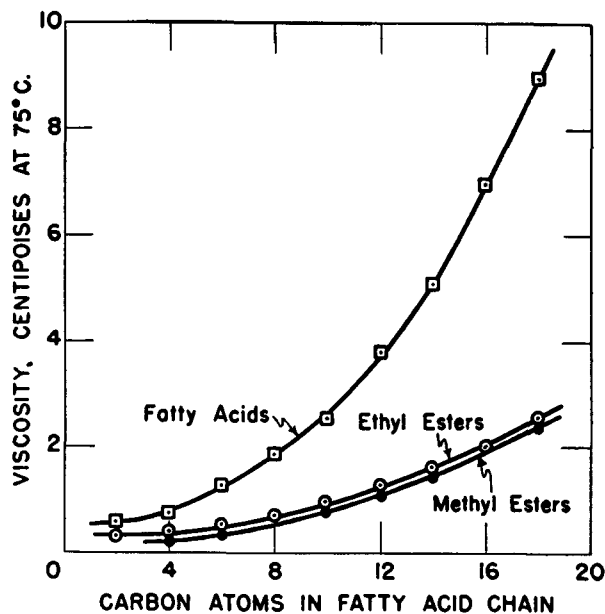Expressed as a logarithmic function, equation (3) becomes

Fig. 2. Viscosities of n-fatty acids and their methyl and ethyl esters.

$$\log \eta = \frac{E}{RT} + \log A \qquad (4)$$

By plotting log η against $1/T$, values for E and A can be determined. It is found that, for a homologous series, E and A are functions of the chain length. Mumford (33) has shown that when either E or A is plotted against the number of carbon atoms in the chain for n-alkanes from C_5 to C_{36}, the resulting graph consists of two straight lines intersecting at the C_{16} point. Since E is a measure of the strength of intermolecular forces existing between molecules of the liquid, this result shows that n-alkanes of chain-length C_{16} and above are apparently subject to smaller forces than would have been predicted from the properties of molecules with shorter chain length.

For ethyl esters of n-alkanoic acids, this change occurs near C_{13} (ethyl tridecanoate). On the basis of the limited data available, this change appears to
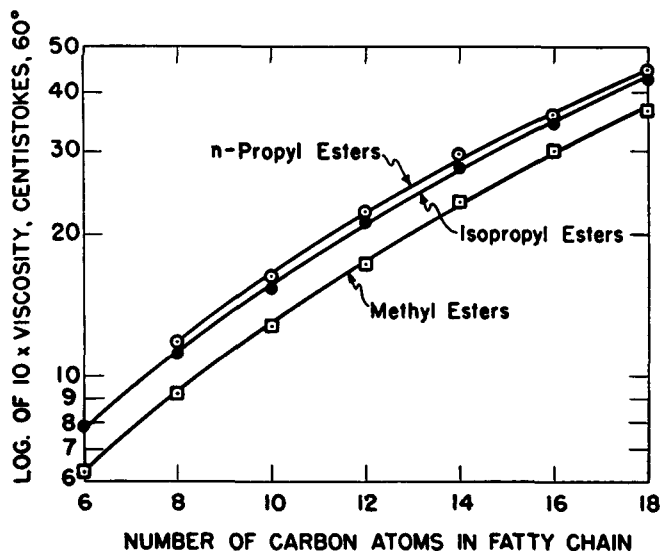

Fig. 3. Viscosities of esters of n-fatty acids.

occur between C_8 and C_{16} for the n-alkanols while, for the free n-alkanoic acids, the plots are approximately linear and without discontinuity over the range of C_4 to C_{18}.

Viscosity data in the range of 120–200° F. for lauric, palmitic, stearic, and oleic acids have been reported by Kern and Van Nostrand (25). Accurate information on viscosities of fatty acids at these higher temperatures is valuable in the study of heat-transfer characteristics of fatty acids and in making engineering calculations in connection with processing fatty acids.

The viscosity of oleic acid increases with increasing pressure. According to Bridgman (6), the viscosity of oleic acid under a pressure of 1,000 kg./sq. cm. is about 4.1 times larger than its viscosity at 1 kg./sq. cm.

Effect of Unsaturation. If, instead of considering the homologous series of fatty acids, we turn to the isologous series of C_{18} fatty acids, *i.e.*, stearic, oleic, linoleic, and linolenic acids, it is found (23) that viscosity decreases with an increase in the number of isolated double bonds. Ravich (37) has shown that the viscosities of these acids and their mixtures vary at constant temperature with the iodine number in accordance with the equation

$$\eta = \eta_0 - KI \qquad (5)$$

where K is a constant, I is the iodine number, and η_0 is the viscosity for $I = 0$ (*i.e.*, for stearic acid).

The viscosity of a *trans* isomer appears to be somewhat higher than the corresponding *cis* isomer. Conjugation increases viscosity although the magnitude of this effect is difficult to determine accurately because a slight amount of polymerization will produce a substantial increase in viscosity. Numerical data (42) showing viscosities for methyl esters of several unsaturated fatty acids are given in Table I.

Association and Orientation of Molecules. Molecules containing strongly polar groups such as carboxyl or hydroxyl groups tend to associate with one another as a result of hydrogen bonding. This effect is responsible for the higher viscosities shown in fatty acids as compared with esters and for the higher viscosities of ricinoleates (Table I) as compared with oleates.

The viscosities of solutions of fatty acids and their derivatives are related to molecular weight by the equation

$$M = \frac{\log \eta_r}{c} \times K_{cm}$$

where M is the molecular weight of the solute, η_r is the relative viscosity $[\eta_r = \eta_{sp} + 1 ; \eta_{sp} = (\eta_c - \eta_0)/\eta_0$, where η_c is the viscosity of the solution and η_0 that of the solvent], C is the molar concentration, and K_{cm} is a constant. Kemp and Peters (24) measured the viscosities of palmitic and stearic acids and their methyl

TABLE I
Viscosities at 14° for Methyl Esters of Unsaturated Fatty Acids

Acid	$\frac{\eta}{H_2O = 1}$
Linolenic	5.0
Linoleic	6.9
Oleic	10.2
Ricinoleic	13.5
Iso-eleostearic	15.8
α-Eleostearate	20.3

esters in *n*-hexane and found that K_{cm} for the acid was about 0.5 the value for the esters. It was concluded that the acids were associated in bimolecular chains in solution.

Meier (29) studied the viscosities of solutions of methyl esters of oleic, linoleic, eleostearic, licanic, ricinoleic, dehydrated ricinoleic, and linseed fatty acids. Below an ester concentration of 25% all viscosities were alike. As the ester concentration was increased above this level, the viscosities of solutions of the nonconjugated esters rose moderately, but solutions of the conjugated esters and especially the hydroxyl- and carbonyl-containing esters showed sharp increases in viscosity. These results may be attributed to association of the polar molecules in the more concentrated solutions. Conjugated bonds are seen to exert an attractive effect similar to that shown by the polar hydroxyl and carbonyl groups.

Another type of associative effect was observed by Cowan and Teeter (10). In comparing the viscosities of pyridine solutions of zinc stearate and zinc dilinoleate, it was found that in dilute solution the viscosity of the zinc dilinoleate solution was approximately the same as that of the zinc stearate solution whereas in more concentrated solutions the viscosity of the zinc dilinoleate solution increased much more rapidly with concentration than that of the zinc stearate solution (Figure 4). These results are attributed to association of the divalent zinc and dilinoleate ions into long chains in the more concentrated solutions.

Kimura (26) found that the viscosity of a solution of lauric, myristic, palmitic, stearic, oleic, or elaidic acids or of a solution of cetyl alcohol was increased in an electrical field. This phenomenon is attributed to orientation of the polar molecules in the electrical field.
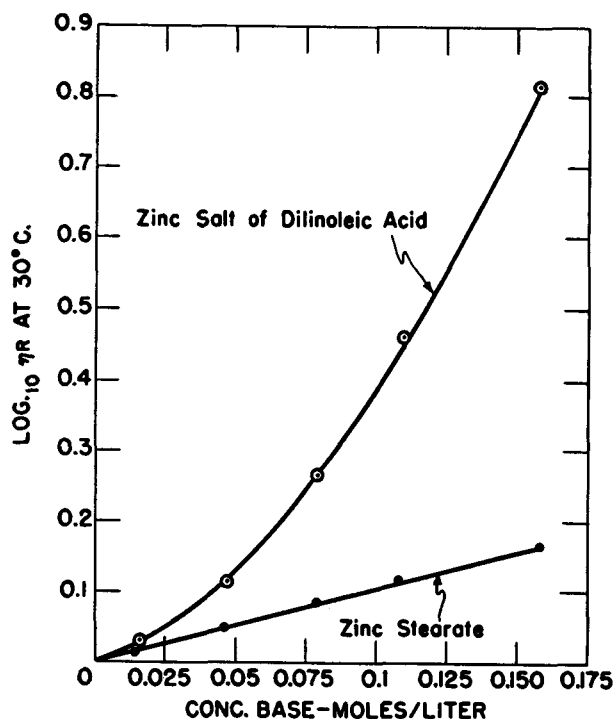

FIG. 4. Relative viscosities of zinc salts in pyridine.
(Figure reproduced by courtesy of
Industrial and Engineering Chemistry)

Viscosity and Chemical Change

Polymerization. The increase in viscosity of unsaturated fatty acid derivatives during thermal polymerization is well known. In a study of the polymerization of dehydrated castor oil von Mikusch (43) showed that the logarithm of the viscosity of an oil bodied at constant temperature was proportional to the length of time of bodying. Cannegieter (8) showed that, if two samples of the same oil bodied at the same temperature but for different lengths of time are compared, the following relationship is obeyed:

$$K = \frac{\log \eta_2 - \log \eta_1}{T_2 - T_1} \qquad (6)$$

where K is a constant and η_1 and T_1 and η_2 and T_2 are viscosity and length of time of bodying for the first and second sample of oil, respectively. The constants, K, obtained for different oils can be used to compare the polymerizability of these oils. For a given oil, K can be used to calculate the time required to obtain a given viscosity or to calculate the viscosity that will be reached after a given period of bodying.

Anderson and Porter (2), in a study of the viscosities obtained by polymerizing samples of linseed, soybean, and other oils and mixtures, showed that three values of K are required to account for the results. One value of K applied to the initial stages of the polymerization, a second value to intermediate stages, and a third value to the final stages. These results are interpreted as indicating the existence of several different types of polymerization reactions.

On the basis of empirical relationships developed by Sims (39), the percentage of polymeric glyceride in a polymerized drying oil and the percentages of dimeric, trimeric and *n*-meric esters in the mixed esters obtained by alcoholysis of these oils can be determined from the viscosity of the polymerized oil.

Polymerization of drying oils was carried out in dilute solution by Adams and Powers (1). They found that the iodine value of the polymerized oil was dependent only on time and temperature. The viscosity of the product was however less when polymerization was carried out in more dilute solutions. The formation of intrapolymers between unsaturated fatty acid chains on the same glyceride molecule is postulated to explain this result. The presence of intrapolymers in heat-bodied linseed oil has been demonstrated by Paschke and Wheeler (35).

Oxidation. The viscosities of methyl linoleate, glycol dilinoleate, and linseed oil remain constant at 100° in a nitrogen atmosphere but increase sharply on admission of oxygen (16). This increase is due to the introduction of polar hydroperoxide groups and to the formation of other polar or polymeric decomposition products of the hydroperoxides.

Polycondensation. Viscosity measurements are important in following polycondensation reactions and in estimating the molecular weight of the resulting polymers. This method was employed by Cowan and Wheeler (11) in the study of linear superpolyesters synthesized from glycols and dilinoleic acid. Figure 5 shows the results obtained in the condensation of ethylene glycol and dilinoleic acid.

Polyamide resins, prepared by polycondensation of ethylene diamine and polymeric fatty acids, induce thixotropy when reacted or dispersed at approximately the 5% level in alkyd resin vehicles (44).
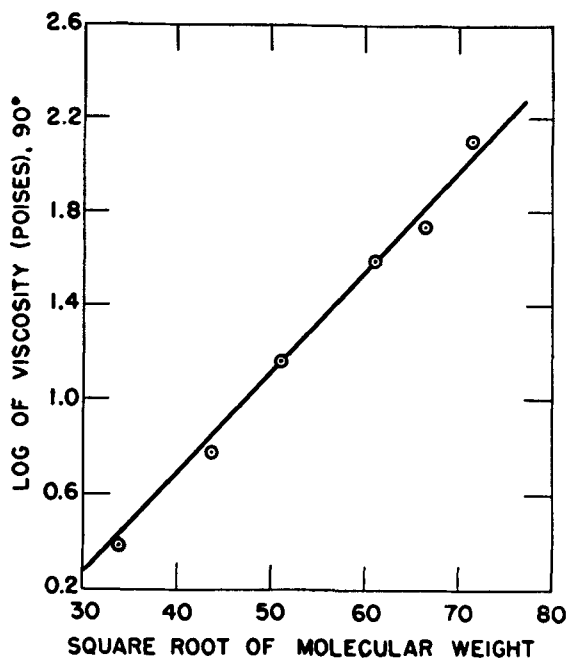
FIG. 5. Viscosity-molecular weight relationship, polyester from dilinoleic acid and ethylene glycol.

Figure 6 shows a typical hysteresis curve obtained in measurement of the viscosity of a polyamide dispersion with the Brookfield viscometer. Vehicles of this type are now receiving much attention in the protective coatings industry.

Higher Fatty Acids and Their Derivatives as Lubricants and Lubricant Additives

The importance of fatty acids and their derivatives in lubrication is shown by the annual consumption of about 100,000,000 lbs. of fats in lubricants (27). While most of these fats are consumed as soaps in greases, fatty acid derivatives are used directly as lubricants for many purposes or as additives to improve the properties of petroleum lubricants.

Boundary Lubrication. Under conditions of boundary lubrication, i.e., low speeds and high specific loads, the viscosity of the lubricant is no longer the principal property determining the effectiveness of the lubricant. Fatty acids and certain of their derivatives are capable of improving the boundary lubricating properties of lubricating fluids. This effect is believed to result from adsorption of the polar end-group of the molecule on the surface of the metal so that the hydrocarbon chain of the molecule is perpendicular to the surface. The polar end-group may combine chemically with the metal to form a soap of a fatty acid or ester, or an alkoxide of a fatty alcohol.

Some of the effects observed in boundary lubrication with fatty acids and their derivatives have been described (5, 20, 30, 38, 40) by Tabor and coworkers. It is found, for example, that an adsorbed film of stearic acid on copper provides boundary lubrication. On heating, the film melts, disorientation occurs, and there is a marked increase in friction. The fatty acid then reacts to form the copper soap, and friction is reduced to a low value. On further heating a permanent increase in friction occurs at the softening point of the soap. At still higher temperatures further deterioration will occur as a result of desorption.

On a non-reactive metal such as platinum, permanent increase in friction occurs above the melting point of the fatty acid.

The total complex of properties displayed under boundary conditions by a lubricating oil is frequently referred to as "oiliness" or "film strength." Fatty acid derivatives utilized commercially to improve the oiliness of lubricants include (27) esters, *e.g.*, butyl oleate, chlorinated stearic acid, free fatty acids, amines, and nitriles.

Lubricant Additives. Certain higher fatty acid derivatives have the property, when added in small amounts to petroleum oils, of depressing the pour-point and increasing the viscosity index. A low pour-point and high viscosity index are important properties of any lubricant that must remain effective over a wide range of temperature, for example, an engine oil. The fatty acid derivative used for this purpose is generally a polymeric derivative of some type. Kuhn (27) indicates that polymers of esters of higher fatty alcohols with methacrylic acid are commonly used as viscosity index improvers in lubricating oils. An extensive literature, particularly patent literature, exists on this subject. It is beyond the scope of this paper to discuss this literature extensively. The following examples will however serve to illustrate some of the types of fatty acid derivatives proposed as pour-point depressants and viscosity index improvers:

1. copolymer of vinyl acetate and the ester of sorbic acid and hydrogenated coconut fatty alcohols (3);
2. polyvinyl palmitate and stearate (36);
3. a heat-condensation polymer of stearic acid (28);
4. copolymers of higher fatty alcohol esters of acrylic and maleic-type acids (34);
5. a copolymer of maleic anhydride and allyl laurate esterified with a C_8-C_{18} alcohol (17); and
6. polyester of decamethylene glycol and dilinoleic acid (45).

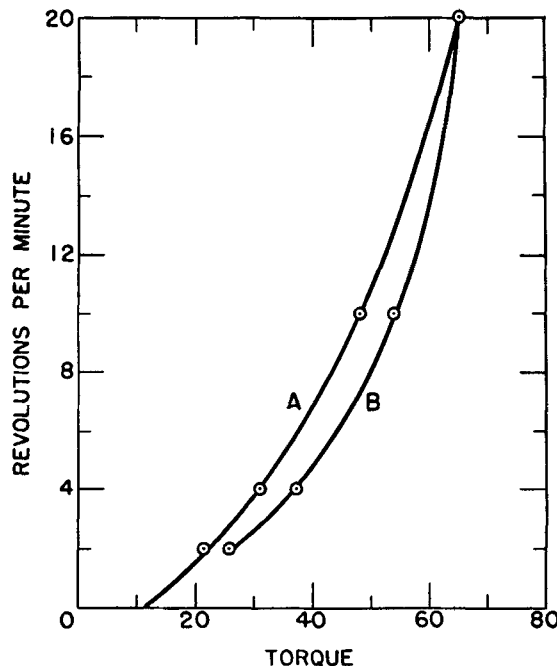The data (9) shown in Table II illustrate the effect of additives on the viscosity index of a petroleum,

FIG. 6. Thixotropy of alkyd resin vehicle modified with polyamide resin. Curve A: decreasing r.p.m. of Brookfield viscometer. Curve B: increasing r.p.m. (44).

TABLE II

Effect of Polyester Additives on the Viscosity Index of a Hydraulic Fluid Oil

Additive [a] %	Molecular weight [b]	Kinematic viscosity centistokes at 100°F.	Kinematic viscosity centistokes at 210°F.	Viscosity Index [c]	Cloud test °C.
0	......	3.17	1.22	100 [d]	....
2	13,200	4.28	1.58	134 [d]	Cloudy, —70°
4	13,200	5.67	2.00	155	Cloudy, —70°
6	13,200	7.67	2.59	183	Cloudy, —65°
8	13,200	9.99	3.26	207	Cloudy, —65°
10	13,200	12.91	4.02	223	Cloudy, —65°
10	8,100	9.87	3.13	194	Clear, —70°
10	11,200	12.37	3.84	217	Clear, —70°
10	14,200	13.98	4.31	222	Clear, —70°

[a] Polyesters from soybean dimeric fat glycols and dimeric fat esters.
[b] End-group titration.
[c] See Ref. 12.
[d] Calculated from equations 5 and 6 of Ref. 12.

having several different molecular weights and prepared by polycondensation of dimeric soybean fat esters and the glycol obtained by hydrogenation of these dimeric esters.

Synthetic Lubricants. Synthetic paraffin lubricants may be prepared from fatty acids by decarboxylation to form hydrocarbons and ketones and subsequent hydrogenation or condensation with aromatic hydrocarbons to yield hydrocarbon products suitable as lubricants. Processes such as this have been of little interest in the United States but have been investigated extensively abroad, particularly in countries where petroleum supplies are not abundant. For details of a typical example of this type of process see Reference 31.

Synthetic Low Temperature Lubricants. Modern military aircraft, instruments, artillery, and other equipment require lubricants having extremely low pour-points ($\leq -65°F.$) and high viscosity indices. The requirements are so exacting that they cannot be met by the use of petroleum lubricants and additives. Extensive research during World War II showed that these requirements could be met by use of synthetic ester-type lubricants such as bis (2-ethylhexyl) sebacate and azelate. Zisman and coworkers have summarized (7) the physical and chemical properties of a large number of pure diesters that are of interest as synthetic lubricating fluids. Several generalizations describing the effect of chain length, branching, cyclic groups, unsaturation, and functional substituents on the viscosity and viscosity temperature characteristics of liquids were developed. These generalizations led to the conclusion that aliphatic diesters with short alkyl branches would be most suitable as lubricants.

Although sebacic acid is obtained from castor oil and azelaic acid is obtained by oxidative splitting of oleic acid, none of the diesters reported by Zisman or others working in this field were higher fatty acid

derivatives in the sense that they contained intact a higher fatty acid chain. Certain diesters of undecyl, tetradecyl, and heptadecyl alcohols with dibasic acids were studied, but these have excessively long chain lengths to possess suitable low temperature viscosity characteristics.

Morgan had described (32) lubricants comprising alkyl esters of acetyl ricinoleic acid. These esters were reported to have a low temperature coefficient of viscosity, but their viscosities at sub-zero temperatures appeared too high. Glavis (19) found that the viscometric properties of ricinoleate esters could be improved by polymeric additives.

It was of interest to attempt to apply the principles established by the work on esters of sebacic, azelaic, and other dibasic acids to the problem of modification of a C_{18} fatty acid chain to obtain products having desirable viscosity-temperature characteristics. A study of these characteristics for a large number of diesters of hydroxy- and polyhydroxy stearic acids was made by Teeter and coworkers (15, 41).

A summary of the properties of a number of these diesters is given in Tables III and IV.

TABLE IV

Viscometric Properties of Diesters

$$CH_3(CH_2)_7 \, CH — CH(CH_2)_7CO_2R'$$
$$\overset{|}{OR} \quad \overset{|}{OCR''}$$
$$\overset{\|}{O}$$

R	R''	R'	Viscosity, Cs. 100°F.	Viscosity, Cs. 210°F.	Viscosity index	ASTM slope	Pour point °F.
CH₃	C₂H₅	CH₃	15.05	3.25	86.5	0.780	< -70
CH₃	C₂H₅	Iso-C₃H₇	17.02	3.60	100.2	0.763	—26
CH₃	C₂H₅	n-C₄H₉	17.52	3.81	123.9	0.740	—69
CH₃	C₂H₅	Iso-C₃H₇	19.58	4.00	115.3	0.750	—64
CH₃	C₂H₅	2-Ethylhexyl	25.06	4.78	125.0	0.730	—64
C₂H₅	C₂H₅	C₂H₅	15.83	3.48	110.8	0.756	—68
C₂H₅	CH₃	C₂H₅	17.52	3.57	89.5	0.788	—65
n-C₃H₇	C₂H₅	n-C₃H₇	18.09	3.89	124.8	0.742	—71
n-C₃H₇	CH₃	n-C₃H₇	20.34	3.98	102.0	0.768	—70
CH₃	n-C₈H₁₇	CH₃	19.89	4.19	132.8	0.726	35 [a]
CH₃CO	CH₃	CH₃	31.64	4.51	25.6	0.818	—6
C₂H₅CO	C₂H₅	CH₃	19.6	3.77	81.4	0.781	—64
C₂H₅CO	C₂H₅	2-Ethylhexyl	33.6	5.57	114.0	0.731	—57

[a] Freezing point.

Derivatives having pour-points below —70°F. were obtained. Other diesters studied had viscosity indices (2a) as high as 155.3 and ASTM slopes (2a) as low as 0.682. It did not prove possible to combine these properties in a single compound or, in derivatives having low pour-points, to obtain a compound having a viscosity of 9,000 cs. or less at —65°F.

This difficulty may be attributed to a fundamental structural obstacle, namely, the fixed linear chain of 18 carbon atoms present in the original fatty acids. Thus it was found that addition to this chain of necessary groups to secure low pour-points resulted in

TABLE III

Viscometric Properties of Diesters

CH₃(CH₂)xCH(CH₂)₁₅₋ₓCO₂R' OR			Viscosity, Cs.	Viscosity, Cs.	Viscosity index	ASTM slope	Pour-point or melting point
R	R'	x	100°F.	210°F.			
Acetyl	2-Ethylhexyl	7(8)	17.92	3.94	134.6	0.722	—44
Propionyl	2-Ethylhexyl	7(8)	17 32	3.92	142.0	0.721	—47
Diethylacetyl	2-Ethylhexyl	7(8)	18.76	4.16	145.9	0.706	—51
Acetyl	2-Ethylhexyl	5	19.46	4.24	145.5	0.699	—63
Propionyl	2-Ethylhexyl	5	17.86	4.09	152.3	0.700	—62
Butyryl	2-Ethylhexyl	5	19.79	4.42	155.3	0.683	—31(m.p.)
Diethylacetyl	2-Ethylhexyl	5	24.33	4.99	145.2	0.682	—22
Propionyl	Methyl	5	10.5	2.75	115.8	0.753	34(m.p.)

undesired increases in viscosity. On the other hand, where a low pour-point could be obtained by introduction of small substituents, the viscosity index was excessively low.

Although none of these diesters turned out to have characteristics that would justify their use as replacements for bis (2-ethylhexyl) sebacate, they represent considerable improvements over earlier materials based on higher fatty acids.

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Conversion of Dianilinogossypol to Pure Gossypol

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ANILINE reacts readily with gossypol, under certain conditions giving quantitative yields of dianilinogossypol. This is a condensation reaction in which water is split out from the amino hydrogen atoms of two molecules of aniline and the oxygen atoms of the two carbonyl groups of gossypol. Dianilinogossypol is a relatively stable compound and is only sparingly soluble in most organic solvents at ordinary temperatures. Because of these properties aniline has been used to recover gossypol from extracts of cotton seed (1, 2, 3).

Unlike gossypol-acetic acid, which is readily dissociated to gossypol and acetic acid, dianilinogossypol is relatively resistant to splitting into its component parts. The literature describes three reagents by which its decomposition has been effected: a) with alcoholic potash, b) concentrated sulfuric acid, and c) with acetic anhydride. With all of these reagents the objective was to remove the liberated aniline by distillation or to change the aniline into chemical compounds which are no longer capable of recombining with the gossypol formed. None of these procedures has been found entirely suitable for the recovery of larger quantities of pure gossypol.

In the present work it was desired to develop a procedure involving a mild treatment in order to protect the reactive gossypol molecule from decomposition so as to improve the yield of gossypol. Considerable difficulty was experienced in the search for a solvent which would separate gossypol and aniline following alkaline hydrolysis, because of the rapidity with which gossypol and aniline recombined. Excellent results were obtained however by rapidly hydrolyzing dianilinogossypol with alcoholic potash diluted with water, followed immediately by cooling and acidification with dilute, aqueous mineral acid which precipitated the gossypol and left the aniline in the aqueous solution as a salt. Following are the details of this procedure.

Hydrolysis of Dianilinogossypol

To 25 g. of powdered dianilinogossypol in a 1-liter Florence flask were added 300 ml. of hot (50°C.) half normal ethanolic potassium hydroxide (in 95% ethanol). Next 0.2 g. of sodium hydrosulfite ($Na_2S_2O_4$) was added, and the mixture was swirled for ½ min. to dissolve essentially all of the solid material. Then 240 ml. of water (80–90°C.), to which 0.25 g. of $Na_2S_2O_4$ had just been added, were poured into the flask, which was then heated by immersion in a steam bath for 8 to 10 min. (4 to 5 min. to heat to the boiling point followed by 4 to 5 min. of boiling). One tenth gram of $Na_2S_2O_4$ was added, the flask was closed, and the contents were cooled rapidly to 50°C. The mixture was acidified with 210 ml. of normal hydrochloric