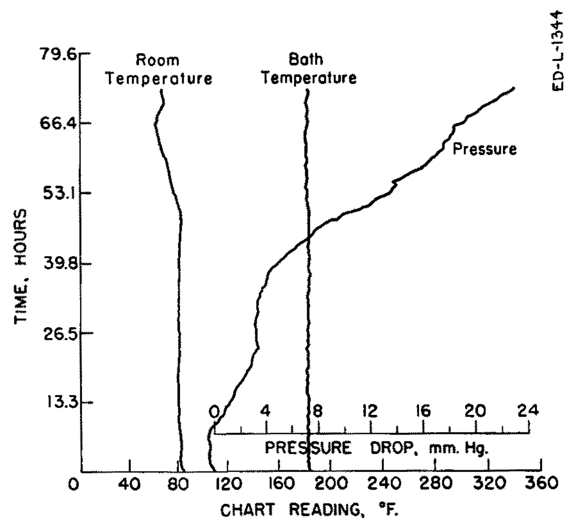

FIG. 4. An oxidation curve obtained with the inductive apparatus.

at the instrument. The recorder was attached to a timing clock so that a complete cycle was printed only once every half hour. The graph represents a 73-hr. run. It will be noted that the upper portion of the curve appears to deviate from linearity. This is due to the fact that the printed points for e.m.f. reflect changes in temperature at the cold junction. If the cold-junction compensator had been removed from the instrument, a straighter curve would have been obtained; but the bath temperature curve then would have shown a deflection due to changes in the ambient temperature. From this curve the major break-point can be easily seen. Approximate calculations to convert scale readings to standard cc. of oxygen absorbed indicate that, on this curve, a 100-degree change represents 2.1 cc. absorption. Since a 1-g. sample was used, the break-point occurred after about 0.8 cc. per gram was absorbed, and at a time of about 38 hrs.

The entire apparatus is extremely simple and thus requires only a moderate amount of care in the operation. The simplifications employed do introduce questions as to the theoretical accuracy of the system. For example, the use of atmospheric pressure as a reference for the pressure changes which occur in the closed flask will cause some fluctuation due to barometric pressure changes. The magnitude of change is a characteristic of the system design, and its effects can be computed. For the curve shown in Figure 4, a 1-in. change in barometric pressure will cause a 4-mm. change in mercury level, or about 6% of the total change observed. For extremely precise measurement therefore the system should be modified or the readings corrected for the fluctuations in barometer, line voltage and frequency, instrument calibration, and so forth. Where determination of the absolute magnitude of oxygen absorption is of minor importance in relation to determination of the time at which the change of rate or break-point occurs, the additional expense of including these refinements becomes unwarranted.

Summary

Two sensitive but inexpensive electrical circuits have been described which translate change in mercury level in a manometer to an electromotive force of sufficient magnitude so that it may be applied to a standard d.c. potentiometric recorder. The recording manometer, when coupled with a simple closed system containing a small amount of lipid material and oxygen or air, can be adapted to determine continuously the cumulative absorption of oxygen by the oil or fat. The break-point, a measure of the stability of the sample, may be obtained from the resulting curve. The apparatus has been successfully employed to determine the oxidative stability of hydrogenated soybean oil, and because of the small amount of attention required, it should be readily adaptable to quality control of edible oil and fat products. The recording manometer should be useful also for measuring and recording pressure changes in other systems.

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Fractionation of Heat-Bodied Linseed Oil with Urea and Acetone

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THE POSSIBLE MODES of heat polymerization are numerous, and the mechanism of polymerization proposed by Kapplemeier (1) and Scheiber (2) is generally accepted. However there is not much unanimity of opinion about the constitution of products formed during the reaction. Such studies are complicated by the fact that mixed glycerides undergo inter- and intramolecular reactions besides cyclization to form complex linear and three-dimensional polymers.

Many workers have investigated the principal reactions that take place during the heat-bodying of oils containing triglycerides that have two or more polyene fatty acid groups. The reaction may be intermolecular between the fatty acid components of two different glycerides or may be intramolecular between two fatty acid components of the same glyceride molecule, resulting in the formation of an intrapolymer (intradimer) and some loss in unsaturation. The intramolecular reaction may also take place in a single fatty acid component of a triglyceride molecule. Hydrolysis of this product yields a cyclic monomer fatty acid. The rate of the polymerization reaction is measured by the drop in iodine value and increase in the molecular weight. Generally the molecular weights are found to be lower than that which would be expected from the change in iodine value. In the earlier stages of the reaction the decrease in iodine value is great, but there is no corresponding increase in molecular weight.

Bradley and coworkers (3, 4), Adams and Powers (5), Barker, Crawford, and Hilditch (6), Ault, Kass, Cowan, and Jackson (7), and Wiseblatt, Wells, and Common (8) suggest that the intramolecular reaction between two fatty acids in the same glyceride molecule predominates in the early stages of reaction and accounts for the initially rapid fall of iodine value. Wiseblatt, Wells, and Common calculated the hypothetical percentage of dimeric acids in the heat-bodied linseed oil. These values and observed percentages of dimeric acids were plotted against the mean molecular weights of the bodied oil. Because these two curves did not coincide, the existence of intramolecular linkages (intradimerization) was indicated. Hence Wiseblatt *et al.* concluded that intradimerization occurred during the earlier stages of heat-bodying. They did not estimate the extent of intradimerization in the monomeric fraction of the bodied oil by separating monomeric and polymeric glycerides.

Joubert and Sutton (9) fractionated Pilchard stand-oil by molecular distillation and found that the non-polymeric triglycerides contained very low proportions of fatty acids linked together (intradimerization) although an appreciable amount of intradimerization was noticed in the sub-fraction of the lowest molecular weight polymer. Boelhouwer, Jol, and Waterman (10) have also stated that little intradimerization between two fatty acid chains occurs during the earlier stages of reaction.

Besides the occurrence of these intra- and intermolecular reactions during the course of polymerization, there may be cyclization within a single fatty acid radical containing two or more double bonds. Steger and Van Loon (11) observed the formation of about 10% of cyclic esters during the polymerization of ethyl linolenate. Sutton (12) attributed the excessive loss of unsaturation to cyclization changes in the fatty acid chains and suggested that the initial sharp decrease in iodine value may be due to the cyclization of the linoleic and linolenic acids in the earlier stages of reaction. During the course of polymerization of methyl linoleate Paschke and Wheeler (13) observed the formation of 15–20% of a monomer which was neither a conjugated nor a normal ester and suggested that this was a cyclic monoethenoid isomer of methyl linoleate. Waterman, Cordia, and Pennekamp (14) also found in the heat-polymerized methyl esters of linseed oil fatty acids that the polymer esters contain on an average about three rings per molecule. After the monomeric portion had been hydrogenated and saponified, the fatty acids were fractionated by the lead-salt-alcohol method. Because the liquid fatty acids fraction was found to contain about one ring per molecule, Waterman *et al.* concluded that the monomeric products were also partly cyclic.

Such fractionation techniques as liquid-liquid-extraction, molecular distillation, and paper chromatography have been used for separating the products and interpreting the chemical changes that occur during heat-bodying of drying oils. McQuillen and Woodward (15) used hot and cold acetone for stand-oil fractionation. They found a large difference in the proportion of the material extractable with hot and cold acetone, *e. g.*, 53.8% and 37.6%, respectively. The quantity of acetone-insoluble material increases smoothly and evenly after the original induction period. Privett, McFarlane, and Gass (16) pointed out that because polymerization proceeds according to the level of unsaturation in triglyceride molecule, the products can be selectively fractionated by means of acetone into a series of oils having widely different properties. Rheineck (17) also observed a relationship between the degree of polymerization and solubility in acetone.

A recent development in this field of study is the urea-fractionation method. Urea forms adducts only with straight chain compounds; no adducts are formed with branched chain and cyclic compounds. This method may therefore be used to fractionate stand-oil fatty acids or their methyl or ethyl esters into monomeric and polymeric portions because the monomers, being straight chain compounds, form insoluble adducts. The polymers, cyclic and branched chain products, remain in solution. Knafo and Catravas (18) fractionated stand-oil by crystallizing the polymerized fatty acids with urea. From the ethyl esters of linseed oil, which had been polymerized by heating for 12 hrs. at 275°, Wells and Common (19) separated monomeric and dimeric products by distillation. The distillable and the total esters were then fractionated with urea. The non-adduct-forming fraction of the distillable esters were cyclic compounds.

In the present work samples of linseed oil were bodied for 1.5 to 5 hrs. at 300°C. to viscosities ranging from 25 to 80 poises. The fatty acids obtained from these different oils were fractionated with urea. The theoretical dimeric acid percentages in each case were calculated from the Adams and Powers (20) equation and compared (Table II-a) with the percentages of urea non-adduct-forming fractions. The remarkably higher values of the latter indicate the presence of intramolecular linkings and cyclization. An estimation of the extent of intradimerization and cyclization during the early stages of reaction was obtained by isolating the acetone-soluble fraction from low viscosity-bodied linseed oil, converting this fraction to methyl esters and separating the monomeric and dimeric esters by distillation. Because the acetone soluble portion contained only a small amount of dimeric glycerides, the percentages of dimeric acids resulting from intermolecular reactions could be calculated. Then the difference between the amount of non-distillable esters (dimers) and the calculated percentage of dimeric acids indicates the extent of true intradimerization. In the case of the monomeric fractions the difference was found to be very small.

Methyl esters of the bodied oil were prepared, and the monomeric and polymeric fatty esters were separated by distillation. The total methyl esters as well as the distillable esters were fractionated with urea to isolate the monomeric cyclic compounds.

While this work was in progress, Paschke and Wheeler (21) heat-bodied linseed oil by viscosities of 2.47, 10.3, and 52.1 poises and separated the monomeric and polymeric triglycerides by molecular distillation. The methyl esters of both fractions were analyzed for monomers, dimers, and trimers. Results showed that in the monomeric glycerides from 1.3 to 6% and in the polymeric glycerides from 10 to 20% of the acid groups underwent intradimerization.

TABLE I

Linseed Oil Heated at 300°C.

Sample No.	1	2	3	4	5	6
Viscosities in poises at 27°C.	0.5	2.0	4.0	40.0	80.0	100.0
Iodine value, Wijs 1 hr.	163.0	138.4	131.8	120.2	116.7	116.7
Iodine value drop						
Observed	18.2	42.8	49.4	61.0	64.5	64.5
Theoretical[a]	2.4	3.0	6.8	17.9	23.5	25.0
Molecular weight	918.0	928.0	998.0	1277.0	1484.0	1554.0
Dimeric acids,[b] % calc.	3.1	3.8	8.2	21.0	27.4	29.2
Acetone-soluble oil						
Yield, %	100.0	100.0	80.0	45.2	31.3	31.0
Iodine value, Wijs 1 hr.	163.0	138.4	128.2	128.2	115.8	114.4
Molecular weight	918.0	928.0	964.0	......	950.0	950.0

[a] The I.V. drop calculated from the equation $Y = 57.8 \times 875 (1/880 - 1/Mn.)$ given by Sutton (12).

[b] Per cent dimeric acids calculated $A = 66.7 (1 - A_1/A_n)$ (20).

Mn: Apparent molecular weight.

A_1: Apparent molecular weight of the original triglyceride.

A_n: Apparent molecular weight of the bodied triglycerides.

Experimental

Alkali-refined linseed oil was bodied to high viscosity in the Kestner's laboratory polymerizing kettle under vacuum (10 mm. Hg.-pressure) at 300°C. After the desired temperature and viscosities (Gardner-Holdt bubble method) had been attained, samples were taken and refractive indices, Wijs iodine values, and molecular weights (cryoscopic method, using cyclohexane as solvent) were determined. Data are summarized in Tables I and II-a.

Acetone Fractionation. The samples listed in Table I were extracted with 5 vols. of cold acetone, and the soluble and insoluble portions were separated. Wijs iodine values and molecular weights of the soluble portions were determined. Results are included in Table I.

Urea-Fractionation. From each sample of bodied oil listed in Table II-a the fatty acids were isolated and were then subjected to one of the following methods of fractionation, with urea.

By Stepwise Addition of Urea. To 20 g. of fatty acids from sample 25 (Table II-a) 40 g. of urea and 240 ml. of methanol were added, and the mixture was dissolved by warming on a water bath at 40 to 50°C. Then it was cooled and left overnight at room temperature. The precipitated adduct was removed by filtration through a sintered glass funnel. To the raffinate were added 20 g. of urea and sufficient methanol to adjust the volume to that of the original mixture. The mixture was warmed, cooled, and filtered as before. Treatment with additional 20-g. portions of urea was repeated until there was no further formation of adduct. The adducts and last raffinate were decomposed by treatment with a large excess of hot distilled water and were acidified with dilute hydrochloric acid. Fatty acids were then extracted with ethyl ether and analyzed.

By Decreasing Solvent Method. A mixture of 20 g. of fatty acids from sample 25 (Table II-a), 60 g. of urea, and 540 ml. of methanol was warmed on a water-bath, cooled, and left overnight at room temperature. Because no adduct was obtained, the solution was concentrated to 400 ml., cooled, and left overnight at room temperature. The precipitated adduct was separated, the raffinate was concentrated to 190 ml., and the adduct was removed as before. Further evaporation of the raffinate to 150 ml. gave no more adduct. Fatty acids were recovered from adduct fractions and raffinate by the procedure outlined above.

The results of the above two methods are given in Table II-b.

Separation by Single Addition of Urea. To each g. of the mixed fatty acids from heat-bodied oil samples 21–25 (Table II-a) were added 4 g. of urea and 4 ml. of methanol. The mixture was warmed on a water bath at 50°C. for half an hour, cooled, and left overnight at room temperature. The adduct was filtered off and washed with 100 ml. of cold saturated urea-methanol solution; the washings were collected in the raffinate portion. The fatty acids from the adduct and raffinate were recovered as before. The percentage yields and Wijs iodine values are given in Table II-a.

Linseed oil was bodied to a low-viscosity range under the atmosphere of carbon dioxide at 300°C., and each half hour after the oil had attained the temperature a sample was withdrawn. The analytical data

TABLE II(a)

Linseed Oil Heated at 300°C.

Sample No.	21[a]	22	23	24	25
Heating time in hrs.	0	3.0	3.5	4.0	4.5
Viscosity in poises at 27°C.	0.50	25.0	40.0	60.0	80.0
Refractive index at 27°C.	1.4799	1.4866	1.4872	1.4881	1.4890
Iodine value, Wijs ½ hr.	181.2	115.0	110.8	107.4	105.0
Molecular weights, corrected for F.F.A.	875.0	1190.0	1306.0	1443.0	1681.0
Dimeric acids, % calc.	....	15.7	19.9	23.5	28.0
Iodine value (Wijs) of total fatty acids	190.1	117.4	114.0	109.6	107.6
Adduct-forming acids					
Yield, %	86.0	38.0	35.2	33.4	30.1
Iodine value					
Found	177.2	81.7	71.0	65.0	62.0
Calculated[c]	175.5	79.3	71.1	65.2	59.5
Composition, % calc.[b]					
Saturated	10.2	10.2	10.2	10.2	10.2
Oleic	22.2	22.2	22.2	22.2	19.9
Linoleic	15.7	5.6	2.8	1.0	....
Linolenic	51.9	....	....	....	....
Non-adduct-forming acids, %	14.0	62.0	64.8	66.6	69.9

[a] Sample No. 21 is original linseed oil.

[b] Calculated from Painter's (24) formula.

[c] The I.V's. are calculated from the calculated composition of adduct-forming fractions, assuming that the amount of the saturated acids remain the same throughout and that the change in oleic acid content is very small.

TABLE III

Linseed Oil Heated at 300°C. Under CO_2

Sample No.	Heating time (hours)	Viscosity in poises at 28°C.	Refractive index 28°C.	Acid value	Iodine value (Wijs 1 hr.)	Molecular Weight	
						Determined	Corrected[a]
21 (Original)	....	....	1.4799	....	181.2	875.0	....
31	1.5	0.75	1.4809	3.20	165.0	898.0	907.0
32	2.0	3.3	1.4848	8.70	134.8	1008.0	1046.0
33	2.5	9.7	1.4870	11.40	121.1	1061.0	1120.0

[a] Molecular weights corrected for the free fatty acids present.

are given in Table III. All three samples, 31–33, of the bodied oil were hydrolyzed and then converted to their methyl esters (samples 41–43), according to the method of Bradley and Johnston (4). The methyl esters were distilled under 10 mm. Hg. pressure so as to separate the monomeric and polymeric esters. The total methyl esters as well as the distillable esters (samples 51–53) from each sample were separated into adduct and non-adduct-forming fractions by using four times (by weight) of urea and four volumes of methanol. The results and the analytical constants of the fractions obtained from total methyl esters and distillable esters are given in Tables IV and V, respectively.

TABLE II(b)

Urea Fractionation of Fatty Acids from Sample IIa (25)

Fraction No.	Stepwise Addition of Urea Method			Decreasing Solvent Method		
	Fatty acids wt.%	Iodine value	Molecular weight	Fatty acids wt.%	Iodine value	Molecular weight
1	10.8	45.1	565	13.9	47.4	557
2	7.7	60.0	......	17.6	81.3	556
3	7.3	87.7	......	......	......	......
4	1.8	......	......	......	......	......
Total adduct-forming portion	27.6	......	......	31.5	......	......
Non-adduct-forming portion	65.5	120.0	......	64.0	119.4	......

Acetone Fractionation. The acetone-soluble portions from samples of bodied oil listed in Table III were hydrolyzed to fatty acids, and these were converted to methyl esters. The methyl esters were distilled under 10 mm. Hg. pressure to separate the monomeric and dimeric fractions. The results of distillation of these esters and analytical constants of the acetone-soluble oil fractions are given in Table VI. The methyl esters and the distillable esters of acetone-soluble portion of sample 33 (Table III) were subjected to urea fractionation, as mentioned above by using four times (by weight) urea and four times (by volume) methanol. The results are given in Table VII.

Results and Discussion

During the heat-bodying of linseed oil the viscosity, refractive index, and molecular weight increase while the iodine value and solubility in acetone decreases (Tables I and II-a). Molecular weights of the acetone-soluble portions remain fairly constant within the scope of experimental error, ranging from 918 to 950 and thus indicating a monomeric structure (calculated mol. wt., 880). The slight increase in molecular weight may be due to the presence of a small amount of dimeric products. After a certain level has been reached, the quantity of acetone-soluble products (monomers) remains relatively constant, although the viscosity and molecular weight continue to increase (Table I, samples 5 and 6). In other words, although the net amount of polymer becomes practically constant after 4.5 hrs., the polymer size continues to increase. About 31.0% of the acetone-soluble fraction is an unreactive material having an iodine value of 115. Rheineck (17) also observed a constant proportion of acetone-soluble materials during the latter phase of the heat polymerization of linseed oil. Bernstein (22) also isolated 23.7% of unreacted monomers with an I.V. of 113.3 by extracting the gelled linseed oil with propyl alcohol. According to his views, the residual monomeric glyceride should contain saturated, oleic, and linolenic acids. However when sample 25, Table II-a, (viscosity 80 poises) was fractionated with urea, no straight chain linoleic and linolenic acids were found in the adducts. Hence it is suggested that the acetone-soluble portion may contain saturated and oleic acids and cyclic compounds.

TABLE V

Urea Fractionation of Distillable Methyl Esters of Bodied Linseed Oil III (31–33)

Sample No.	51	52	53
Yield %[a]			
Distillable esters	94.0	83.7	67.0
Adduct-forming esters	85.6	66.8	49.3
Non-adduct-forming esters	8.4	16.9	16.7
Cyclized esters (calcd.)	6.0	17.7	17.7
Iodine Value Wijs 1 hr.			
Distillable	157.1	....	113.0
Adduct	158.1	....	100.5
Non-adduct	142.0	139.3	140.6[b]
Refractive Index			
Distillable	1.4651	1.4685	1.4687
Non-adduct	1.4798	1.4802	1.4793
Molecular Weight			
Distillable	292.4	305.3	308.0
Adduct	290.2	294.7	270.0
Non-adduct	301.0	310.0	309.0[c]

[a] Yield calculated on the basis of total methyl esters.
[b] Iodine value, Benham and Klee, 1 hr., 169.1.
[c] Saponification value 194.0.

The iodine value drops rapidly in the earlier stages and slowly at the later stages of reaction. Attempts have been made to correlate the drop in iodine value

TABLE IV

Urea Fractionation of Methyl Esters from Linseed Oil Bodied at 300°C. III (31–33)

Sample No.	Adduct-forming esters, %	Iodine Values			Reefractive Indices at 28°C.		Molecular Weight		
		Total esters	Adduct	Non-adduct esters	Total esters	Adduct	Total esters	Adduct	Non-adduct esters
40 (Original)[a]	98.0	180.3	179.0	260.0	....	....	....	....	....
41	88.0	163.6	166.0	137.0	1.4642	1.4609	297.2	297.8	390.7
42	66.0	130.5	....	....	1.4679	1.4598	316.3	293.2	420.0
43	49.3	117.8	108.0	130.0	1.4698	1.4583	441.0	310.0	549.0

[a] Methyl esters of unbodied linseed oil.

TABLE VI

Acetone-Soluble Fractions of the Polymerized Linseed Oil III (31–33)

Sample No.	61	62	63
Yield, %	100.0	80.8	51.8
Iodine value (Wijs 1 hr.)	165.0	131.8	120.1
Refractive index at 28°C	1.4809	1.4832	1.4833
Molecular weight	898.0	927.6	938.3
Dimeric glycerides[a]	2.80	9.40	11.40
Dimeric acids[b] (A)	2.60	3.80	4.50
Non-distillable esters, % of total (B)	6.0	10.0	11.7
Molecular weight of total esters	292.4	316.3	322.0
Intradimerization, % as acids (B–A)	3.40	6.20	7.20

[a] Percentage of dimeric glycerides present in the acetone-soluble fraction was calculated from the molecular weight of acetone-soluble oil, assuming that only two molecular species were present in this particular fraction.

[b] Percentage of dimeric acids present in acetone-soluble glycerides calculated from their number average molecular weight by using the expression given by Adams and Powers (20).

and the apparent molecular weight. Bernstein (22) found that the number average molecular weight doubled when the drop in iodine value was 56 units, which corresponds to a loss of 1.93 double bonds per oil molecule. Experimental results given in Table I show that the molecular weight was not doubled for a lowering of iodine value by 56 units, *e.g.*, sample 4 had an iodine value 61 units lower than the original oil but the molecular weight was only 1277 instead of the calculated value of 1750 (double the molecular weight of the original glyceride). Although Bradley and other workers (3, 4) from the theoretical point of view suggested that doubling of molecular weight takes place for a lowering of I.V. by 29 units (one double bond per oil molecule), the drop in I.V. is found to be always more than that calculated from the molecular weight because of the intradimerization and cyclization in the fatty acid chains which occur during heat-polymerization. Flory (23) had developed statistical methods based on the degree of probability of intermolecular reactions whereby molecular weight distribution and gelation points in polymerizing systems could be calculated. Sutton (12) stated that these statistical methods could be used with advantage and gave a mathematical relationship between the number of average molecular weight (Mn.) and the decrease in iodine value (Y) exclusively due to intermolecular linkages in the polymerizing oils, assuming that the Diels-Alder mechanism is correct.

$$Y = 57.8 \times 875 \, (1/880 - 1/\text{Mn.})$$

In Table I the decrease in iodine values calculated from the observed number average molecular weights according to this equation are given. The observed drops in Wijs iodine values were much greater than the calculated ones. This extra loss of unsaturation, without a corresponding increase in molecular weight, must have been due partly to conjugation and partly to intradimerization and cyclization reactions.

It is well known that the thermal polymerization of conjugated unsaturated fatty acids proceeds by Diels-Alder reaction. Presumably the double bonds of the non-conjugated fatty acids rearrange into conjugated systems prior to Diels-Alder addition reaction. Generally, as found by Bradley and other workers, about 5 to 6% conjugation occurs in heat-bodying of drying oils in the absence of catalysts. Barker, Crawford, and Hilditch (6) confirmed that the conjugation is about 5 to 6% throughout the polymerization reaction of linseed oil. However this amount of conjugation is insufficient to explain the large drop in iodine values.

In order to investigate further the course of intramolecular reactions during heat-bodying, fatty acids from these oils were fractionated with urea. The amount of urea required for complete separation of monomeric and polymeric products was first determined by fractionating acids from sample 25 (Table II-a) according to two methods: the stepwise addition of urea and decreasing solvent methods (Table II-b).

The losses in the former were more than in the latter method because of the number of steps involved in separation. It is evident from the results given in Table II-b that the quantity of urea required to effect the complete separation of the straight chain compounds is four times (by weight) that of the fatty acids sample. Therefore in the following separations this amount was added in one lot.

In Table II-a are summarized results of urea fractionation of fatty acids from the unbodied oil and from bodied oil samples. The iodine values of the adduct-forming portions from the bodied oil samples do not show the presence of linolenic acid. It is reasonable to believe that the non-adduct-forming fatty acids from oils of viscosities 25 to 80 poises contain very little, if any, unreacted linolenic acid. Hence the non-adduct-forming fractions must contain cyclic compounds and dimeric acids which result from inter- and intradimerization reactions. This hypothesis was strengthened by comparing the compositions of non-adduct-forming fractions with the calculated percentages of dimeric acids. The fatty acid compositions of adduct-forming fractions shown in Table II-a were calculated on the assumptions that saturated acids remain unchanged throughout and that linolenic, linoleic, and oleic acids disappeared during the course of heat-bodying. To check the validity of these assumptions and calculations, the iodine values of the adduct-forming fractions were calculated for the given compositions and agreed with the observed iodine values. Hence it is suggested that polymerization is selective and the most unsaturated component reacts first in polymerization.

In the above discussion intramolecular reactions and cyclization were assumed to be the cause of the decrease in iodine value during polymerization. However additional data were required before the extent of the reactions during the early stages of polymerization could be estimated. Hence mixed methyl esters of heat-bodied oil samples 31–33 (Table III) were fractionated with urea.

TABLE VII

Urea Fractionation of the Methyl Esters from the Acetone-Soluble Portion (III–33)

	Yield[a] %	Iodine value (Wijs, 1 hr.)	Refractive index at 28°C.	Molecular weight
Total mixed methyl esters	....	118.2	....	322.0
Distillable esters (X)	88.3	113.3	....	....
Adduct-forming distillable esters	67.6	....	....	....
Non-adduct-forming ester distillate or cyclized esters	20.7	139.5	1.4798	297.0
Adduct-forming mixed esters (Y)	68.7	117.0	....	....
Non-adduct-forming mixed esters	31.3	125.0	....	....
Cyclized esters (X–Y) calcd	19.6	....	....	....

[a] As % of wt. total esters.

Data in Table III show that 2.5 hrs. of bodying caused a drop in iodine value of 60.1 units although the increase in molecular weight was only 245 units. In samples 31 and 32, which were bodied for 1.5 and 2.0 hrs., respectively, the iodine value drops (16.2 and 46.4) were also too large to account for increases in molecular weight (32 and 171). When methyl esters (samples 41–43) were treated with urea (Table IV), 88.0, 66.0, and 49.3%, respectively formed adducts and therefore were straight chain esters. The non-adduct-forming products must be cyclic or polymeric acids. The iodine values of the adducts and raffinates closely check with the observed values of total methyl esters. Molecular weights of the adduct-forming fractions were determined to confirm their monomeric nature. In Table V are summarized data on the distillation of methyl esters and the urea fractionation of the ester distillates. Although monomeric esters readily form adducts with urea, the methyl ester distillates were not quantitatively precipitated with urea and consequently contained some cyclic products. When the total undistilled esters were similarly treated with urea, the difference between the weight of ester distillate and the weight of undistilled ester precipitated with urea was found to agree closely with the amount of the non-adduct-forming portion of distillable esters.

Because the I. V. of the non-adduct-forming fractions was 140, the presence of cyclic compounds and the virtual absence of triene esters (I.V. 260.9) in this fraction was indicated. Brod, France, and Evans (25) observed some isomerization of ethyl eleostearate probably to a cyclic form during its polymerization. Bradley and Johnston (4), while fractionating the methyl esters of the polymerized linseed oil fatty acids by vacuum distillation, found a high-boiling fraction (B.P. 180–220°C.) amounting to 10%, having I.V. 131.0 (Kaufmann), molecular weight 303, saponification value 190.0, refractive index at 25°C. 1.4640, and no conjugation. In order to study further the mechanism of polymerization of linseed oil Bradley and Richardson (26) examined the fractions by ultraviolet absorption methods and concluded that the differences in absorption for the distillates could not be fully explained unless the existence of cyclic monomers formed by intramolecular action was postulated. Data in Table V show that all the non-adduct-forming fractions of the distillable methyl esters have about the same I.V., molecular weights, and refractive indices. The mean unsaturation calculated from the molecular weights and Wijs I.V. is between —3.2 H and —3.4 H, which suggests their dienoic nature. The non-adduct-forming distillate fraction (equal to about 17% of the esters) was found to have I.V. of 169.1 by the Benham and Klee (27) method, and a mean molecular weight of 289 was calculated from the saponification value 194. Wells and Common (19) have also obtained about 11% cyclic esters, having I.V. of 170.7 (Benham and Klee method), molecular weight 300, and refractive index 1.46986. Apparently this product was formed by cyclization of linolenic acid with the disappearance of one double bond.

The acetone-soluble oil consisted chiefly of monomeric glycerides in which two fatty acids of the same glyceride molecule were intramolecularly linked or a single fatty acid had been cyclized, and contained little intermolecularly linked glyceride. The theoretical percentages intermolecularly linked dimeric acids (A) recorded in Table VI were calculated from the molecular weight by using the expression $A = 66.7 \left(1 - \frac{A_1}{A_n}\right)$. The actual percentages of the dimeric esters were found by distillation of the methyl esters (B). The difference between the percentage isolated (B) and the calculated percentages of dimeric acids (A) gives the true extent of intradimerization in the monomeric glycerides. Results of urea fractionation of total and distillable methyl esters from acetone-soluble fraction of heat-bodied oil (sample 63, Table VI) are recorded in Table VII. These data show that in the monomeric fraction 20.7% of the products were cyclic and only 7.2% resulted from intradimerization. Urea separated 68.7% of adduct-forming esters (I.V. 117) and 31.3% of non-adduct-forming esters (I.V. 125).

Because only 3 to 7% intradimerization was observed in the monomeric fraction and 8 to 17% cyclization occurred during the early stages of reaction, the initially rapid fall in I.V. must result from cyclization in the fatty acid chains rather than intradimerization. Hence it is concluded that the cyclization may be the principal cause for the large drop in iodine value during the initial stages of polymerization.

Summary

During heat-bodying of linseed oil at 300°C. the drop in iodine value is high in the initial stages, without a corresponding increase in molecular weight. These changes are due partly to conjugation and partly to intradimerization and cyclization. However the amounts of conjugation (5 to 6%) and intradimerization (3 to 7%) are insufficient to explain the large drop in iodine value. Cyclization of linolenic acid takes place to the extent of 8 to 17% at the earlier stages of polymerization and hence is the principal cause of the large drop in iodine values. This cyclized product of linolenic acid was isolated by urea and characterized by determinations of saponification value, iodine value, and mean molecular weight.

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Synthetic Detergents from Animal Fats. VI. Polymerizable Esters of Alpha-Sulfonated Fatty Acids[1]

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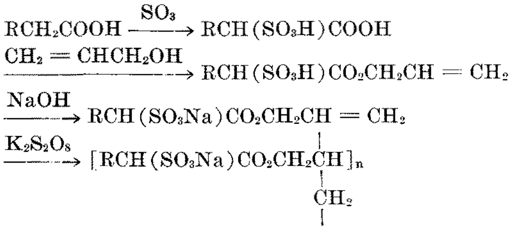
THE EASE of preparation of esters of α-sulfonated saturated fatty acids, such as sodium alkyl α-sulfopalmitates and stearates (4), or disodium 2-sulfoethyl α-sulfopalmitates and stearates (5), has suggested similar esterification with unsaturated alcohols to form polymerizable anionic surface-active agents and detergents. Allyl alcohol was the alcohol selected for this purpose.

Accordingly, sodium allyl α-sulfopalmitate, sodium allyl α-sulfostearate, and their respective polymers were prepared and examined for surface-active and detergent properties.

Reactions involved in the preparation of the monomers and polymers are as follows:



$$\begin{aligned}
&RCH_2COOH \xrightarrow{SO_3} RCH(SO_3H)COOH\\
&\xrightarrow{CH_2 = CHCH_2OH} RCH(SO_3H)CO_2CH_2CH = CH_2\\
&\xrightarrow{NaOH} RCH(SO_3Na)CO_2CH_2CH = CH_2\\
&\xrightarrow{K_2S_2O_8} [RCH(SO_3Na)CO_2CH_2\underset{\substack{|\\ CH_2\\ |}}{\overset{|}{C}}H]_n
\end{aligned}$$

where R is $C_{14}H_{29}$ or $C_{16}H_{33}$ and n is the degree of polymerization.

Sodium Allyl α-Sulfopalmitate

A solution of 0.357 mole (120 g.) of α-sulfopalmitic acid (5), N. E. 163.2 in 500 ml. of allyl alcohol was heated and stirred 6 hrs. at the reflux temperature, neutralized with a solution of sodium hydroxide in aqueous ethanol, and cooled to —25°. The yield of the precipitated ester was 85%. The purity at this point, also about 85%, is adequate for use in surface-active or detergent compositions, or for conversion to the polymer. Crystallization from water to remove unesterified α-sulfopalmitic acid as the sparingly soluble sodium salt, and further crystallization of the ester from methanol gave sodium allyl α-sulfopalmitate as a white solid, m. p. 92.2–93.4°, in a yield of 35%.

Analysis: Calculated for $C_{19}H_{35}NaO_5S$, 57.26% C, 8.88% H, 5.77% Na, 8.05% S, Iodine No. 63.7; found, 56.93, 8.85, 5.68, 8.12, 61.1, respectively.

Sodium Allyl α-Sulfostearate

In a similar manner α-sulfostearic acid (5), N. E. 179.9 was esterified with allyl alcohol, and the purified sodium allyl α-sulfostearate, m.p. 99.2–100.5°, was isolated.

Analysis:[3] Calculated for $C_{21}H_{39}NaO_5S$, 59.12% C, 9.21% H, 5.39% Na, 7.52% S, Iodine No. 59.5; found, 58.97, 9.14, 5.39, 7.40, 58.9, respectively.

Polymerization

The polymerization of sodium allyl α-sulfopalmitate or sodium allyl α-sulfostearate was carried out as follows.

A solution of 75 g. of the monomer and 3.5 g. of potassium persulfate in 700 ml. of water was heated 8 hrs. at 70°. The progress of polymerization was evident by an increase in viscosity; after about 3 hrs. the solutions were too viscous to stir effectively. The polymer was separated by adding 3 volumes of 95% ethanol to 1 volume of the aqueous solution. The precipitated amorphous solid was redissolved in water and again precipitated by the addition of 2 volumes of ethanol. This operation was twice repeated, and the final precipitate was dried in a vacuum oven. The purified polymer was obtained as a light, cream-colored solid in a yield of 70%. The Wijs Iodine No. of the polymer, about 2 to 4, somewhat inexact because of the limited solubility of the polymer in chloroform and glacial acetic acid, indicated a degree of polymerization of the magnitude of 10^1.

Solubility and Viscosity

The monomers are readily soluble and form aqueous solutions of about 20% concentration which may become viscous solutions or gels on standing at room temperature. The polymers form viscous solutions at a concentration of about 2%; and they are practically insoluble in the usual organic solvents.

The viscosity of a 2% aqueous solution of polymerized sodium allyl α-sulfostearate, which has thixotropic properties, was measured with a Brookfield synchroelectric viscometer, using a No. 3 spindle. At 25°, and at speeds of 6, 12, 30, and 60 r.p.m., the viscosity was 3680, 2380, 1430, and 1080 centipoises, respectively. The viscosity of the polymers indicates possible use as a thickening agent.

Different preparations of the same polymer were sometimes found to have quite different viscosities, perhaps because of minor impurities or slight differences in the method of polymerization.

Surface-Active Properties

Values for surface and interfacial tension, wetting and emulsifying properties and calcium stability are recorded in Table I for the monomers and polymers.

The monomers lower the surface tension of water, and the interfacial tension against petrolatum, in a manner similar to that found for sodium alkyl α-sul-

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[3] Microanalyses for C, H, and S performed by Dolores A. McClelland.