is also poor. Our data with DMAB gives a linear relationship with concentration whereas Kolthoff reported an increase in solubilization with increase in concentration. It is interesting to note that Orange OT is solubilized more than DMAB in DDA.HCl while the reverse is true in the case of N-dodecyl- alanine hydrochloride, suggesting a difference in mechanism by which micelles incorporate the dyes of different structures.

Results of Na-oleate agree fairly well with those of McBain (10).

Results using Span 20 indicate that solubilization characteristics are shown by detergents that are dispersible but not soluble in water. However the solubilization is slow, showing only two-thirds of the maximum values after one day of rotation. It is also interesting to note that Tween 20 solubilizes about twice as much DMAB as Orange OT (on molar basis) whereas Span 20 solubilizes the two dyes to about the same extent.

Solubilization data has been used to determine the critical micelle concentration of detergents, by plotting the amount of solubilized dye against detergent concentration. In general, the C.M.C. found by solubilization is of a magnitude comparable to that obtained by other methods, such as pH measurements and the spectral dye procedure. However it is difficult to obtain accurate C.M.C. values because, first, solubilization is not linearly proportional to concentrations above the C.M.C. and a straight line cannot legitimately be drawn to find the intersection on the abscissa or concentration axis, and secondly the nature of solubilization below the C.M.C. is doubtful. Assuming no solubilization below the C.M.C., the C.M.C. found by using data in this work agree well with the values obtained by plotting both Kolthoff's and McBain's data. The C.M.C. for Na-laurate from this work is 0.0275 or 0.0282 M, and our plot of the data of Kolthoff and of McBain gives 0.0275 and 0.027 M, respectively. In contrast, Kolthoff reported a C.M.C. of 0.0253 M from his data and 0.0195 from McBain's data (Table 4).

Summary

1. Solubilization data have been obtained for aqueous solutions of Na-laurate, K- laurate, dodecylamine-HCl, Tween 20, Span 20, N-dodecyl- -alanine-HCl, Na-oleate, Tergitol 4, and Ultrawet K, using the water insoluble dyes, Orange OT, and dimethylaminoazobenzene as the solubilized substances. Results indicate that the dye solubility method is fairly reproducible. Filtration of samples was found to be an important part of the technique.

2. A slight excess of fatty acid or of alkali in Na- and K-laurate solutions was found to have no appreciable effect on solubilization.

3. In agreement with Kolthoff's but not with McBain's findings, the Na- and K-laurates were found to yield the same solubilization of either DMAB or Orange OT, indicating that the solubilizing species in solution depends upon the nature of the long chain ion.

4. Agreement on solubilization for dodecylamine-HCl with previous workers is poor.

5. The present work indicates no solubilization below the critical micelle concentration. The apparent solubilization reported by Kolthoff was attributed to suspended dye.

6. The use of solubilization data in the determination of critical micelle concentration is examined, and values are compared with previous works.

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Preparation of Peroxide Concentrates from Autoxidized Fatty Acid Esters[1,2]

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ALTHOUGH the first relatively concentrated hydroperoxides of fatty materials were isolated by molecular distillation (4), there are several objections to the use of this method for the separation of peroxides from autoxidized fatty acid esters, especially from autoxidized linoleates and linolenates. First, a portion of the peroxides is destroyed by decomposition or other alterations during distillation (10). This, coupled with the difficulty of obtaining good fractionation by molecular distillation, makes it almost impossible to obtain a high yield of the original peroxides in concentrated form.

Swift, Dollear, and O'Connor (11) isolated hydroperoxides from autoxidized methyl oleate in 85 to 90% concentration by a low temperature fractionation procedure in which the unoxidized oleate was segregated by crystallization from acetone at —80° C. The peroxides were recovered from the filtrate and

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[2] This work was supported by a contract between the Office of Naval Research, Department of the Navy, and the University of Minnesota.

represented about 60% of the peroxides originally present. The low temperature employed by these workers insured against any significant changes in the peroxides during concentration, but there was no assurance that the peroxides recovered were truly representative of those originally present. Hence chemical data from such peroxide concentrates might have only limited value in elucidating the course and mechanism of autoxidation. As far as is known, attempts to obtain high yields of linoleate or linolenate hydroperoxides by low temperature crystallization procedures generally have been unsuccessful.

A number of investigations (1, 2, 3, 4) have dealt with the separation and analysis of the products of oxidized fatty acid esters by chromatography. Generally it was found that the oxidized fraction was preferentially adsorbed on alumina from petroleum ether. However, except when very small amounts of material were used and the period of adsorption was short, it appeared that the oxidation products were altered to some extent during the process. Bergström (1) found that linoleate peroxides slowly decomposed when adsorbed on alumina. Dugan and coworkers (3) isolated a small fraction of material from autoxidized linoleate with a peroxide value of 4,000 m.e./kg., using a specially prepared sodium aluminum silicate column, but because a relatively large proportion of oxygenated products other than hydroperoxides were also found, it appears possible that some chemical changes in the autoxidation products had taken place on the column.

Lundberg, Chipault, and Hendrickson (7) reported various analyses of peroxide concentrates from autoxidized methyl linoleate obtained by partition between two solvents. However not all of the original oxidation products were isolated, and there were some indications that the more highly oxidized products of autoxidation were concentrated in the isolated peroxide fraction. More recently, Fugger and coworkers analyzed the products of the autoxidation of methyl oleate (6) and methyl linolenate (5) by countercurrent distribution methods. These investigators distributed the oxidized esters in a 29-tube Craig apparatus and analyzed selected fractions. It is evident from their studies and from the previously reported results of Privett and Lundberg (8) on autoxidized methyl linoleate that the entire oxidized fraction can be separated quite completely from the unoxidized ester by countercurrent distribution methods. Fugger and coworkers did not isolate pure peroxides because their original autoxidized esters contained considerable amounts of secondary reaction products which distributed themselves in varying amounts in all the fractions.

This paper describes a simplified countercurrent extraction process for the separation of fatty peroxides for which no special extraction apparatus is required. The pattern of the distribution is arranged to permit the addition of fresh plates at regular intervals to assure the quantitative separation of the oxidized from the unoxidized fractions. Relatively highly concentrated solutions of autoxidized fatty acid esters (30 to 40%), that ordinarily cannot be used in semiautomatic equipment because of the changes that occur in the relative volumes of the solvent pair, can be readily processed by the method described here.

Experimental

Materials. The fatty acid esters used for these studies were obtained from the Hormel Foundation. The methyl oleate was isolated by a low temperature crystallization procedure and had an iodine value of 85.2 (theoretical 85.6). The methyl linoleate and linolenate were prepared from their corresponding bromostearic acids and had iodine values of 173 (theoretical 172.4) and 260 (theoretical 260.4), respectively. The ultraviolet absorption spectra indicated they were essentially free of conjugated materials.

Autoxidation. In order to minimize secondary reactions it was desirable to conduct the autoxidation at relatively low temperatures. However since methyl oleate autoxidizes very slowly at low temperatures, the oxidation of this ester was carried out by bubbling oxygen through a sample of approximately 100 g. in a bath at 50°C. The autoxidation of methyl linoleate and linolenate was accomplished by keeping approximately 100 g. of ester in the dark at 0 to 2°C. in loosely stoppered 250-ml. Erlenmeyer flasks. The flasks were uncovered and shaken at frequent intervals to replenish the supply of dissolved oxygen. The progress of the oxidation was followed by periodic determinations of the peroxide values.

Peroxide Determination. An iodometric method in which air was excluded at all critical stages was employed in the determination of peroxide values. Then 0.1 to 0.3 g. of autoxidized ester or peroxide concentrate was dissolved in 50 ml. of air-free acetic acid-chloroform (2:1) in a 250-ml. flask; 1 ml. of an air-free saturated aqueous solution of potassium iodide was added, and the flask placed in a water bath at 35° for 30 minutes. Oxygen-free nitrogen was bubbled through the solution continuously during this interval. Fifty ml. of oxygen-free distilled water was then added and the solution titrated with 0.01 N thiosulfate in the usual manner.

Extraction Procedure. The solvent pair was prepared by mixing equal quantities of absolute ethanol and Skellysolve F in a large separatory funnel and adding 7 ml. of distilled water for each 40 ml. of absolute ethanol. Two phases formed on the addition of the water, and in order to assure complete saturation of one phase with the other they were thoroughly mixed before being separated. The hypophase was estimated to consist of about 87% ethanol.

For convenience and in order to follow the progress of concentration of the peroxides the extraction was carried out in stages. The autoxidized ester was dissolved in 200 or more milliliters of the Skellysolve F epiphase and in concentrations as high as 30%. The first stage consisted of exhaustively extracting the peroxides from the Skellysolve solvent in a 500-ml. separatory funnel with successive 100-ml. portions of the ethanol extractant. The 100-ml. portions of the extractant were collected in individual 125-ml. Erlenmeyer flasks and set aside for the second stage. Generally purified nitrogen was bubbled over the solution during the extraction and through each successive extractant as it was collected to avoid any further oxidation. Occasionally it was necessary to add solvent to the Skellysolve F phase during the extraction to maintain the volume of this phase. The progress of the extraction of the peroxides into the extractant was checked by determining the peroxide value on an aliquot of the Skellysolve F phase.

Generally it was only necessary to make two or three analyses to follow the progress of the extraction and to determine how many plates were required for the complete removal of the peroxides from the epiphase. However, to illustrate the stepwise extraction of the peroxides from the initial epiphase, that is the first stage, the experiment shown in Table I was conducted. In this experiment 20 g. of autoxidized methyl linoleate (P.V. 840) were dissolved in 200 ml. of Skellysolve epiphase and extracted with nine 100-ml. portions of the alcohol hypophase. In this instance the manner in which both the unoxidized and oxidized fractions distributed themselves after each plate was determined.

TABLE I

First Stage Concentration of the Peroxides of Autoxidized Methyl Linoleate (P. V. 840)

Plates	Epiphase		Hypophase		Partition Ratio[a]		Peroxides extracted into hypophase
	Unoxidized ester	Oxidized ester	Unoxidized ester	Oxidized ester	Unoxidized ester	Oxidized ester	
	g.	*g.*	*g.*	*g.*			%
Original sample	17.3768	2.7750	.....	.....	.....	.....	.....
1	17.0555	1.5707	0.3213	1.2043	53.10	1.31	43.40
2	16.2976	0.8495	0.7579	0.7212	21.50	1.18	69.50
3	15.5107	0.4560	0.7869	0.3935	19.70	1.16	83.50
4	14.7211	0.2424	0.7896	0.2136	18.70	1.18	91.30
5	13.8701	0.1396	0.8510	0.1028	16.30	1.36	94.00
6	13.0585	0.0798	0.8116	0.0598	16.10	1.33	97.10
7	12.3341	0.0484	0.7244	0.0314	17.10	1.54	98.30
8	11.6319	0.0306	0.7022	0.0178	16.60	1.72	99.00
9	11.0035	0.0214	0.6284	0.0092	17.50	2.33	99.30
Totals	11.0035	0.0214	6.3733	2.7536	.....	.....	99.30

[a] Partition ratio: grams in epiphase/grams in hypophase.

Although the two phases separated immediately after they were thoroughly mixed, it was doubtful that complete equilibrium with respect to the migration of the solutes was established in all plates, especially in those in which the concentration of materials was high. Nevertheless the hypophase in each plate was withdrawn as soon as the two phases separated, as it was not practical and was not found necessary to have complete equilibrium conditions established. Under these conditions there were some variations in the partition ratios and likewise in the number of plates and stages required for a given separation. Although the large and extremely favorable partition ratio in the first stage is thus undoubtedly not a true value for these concentrations of materials, nevertheless the extraction of the peroxides progresses in a uniform pattern, as shown in Table I, and in practice only two or three analyses are required to determine the number of plates required for complete removal of the peroxides from the epiphase.

It may be observed (Table I) that while the partition ratio of the oxidized fraction from the second through the nine plates required for the relatively complete extraction of the peroxides almost doubled (1.18-2.33), that of the unoxidized fraction changed only from 21.5 to 17.5. This relative preference of the peroxides for the alcohol hypophase indicates that the last traces of peroxides may be separated from the unoxidized ester. In fact, in this experiment (Table I), which is representative of the first stage of a typical run, 99.3% of the peroxides were extracted into the hypophases, leaving approximately 63% of the unoxidized ester in the epiphase essentially free of peroxides (less than 0.2% peroxides). Since the partition ratio of the peroxides was still highly favorable, an even finer separation might have been obtained, if desired, by applying additional plates. The segregation of 63% of the unoxidized ester in the epiphase results in a proportionate concentration of the peroxides in the hypophases. The peroxides, in fact, may be completely concentrated, as will be shown in subsequent runs, by employing more stages to segregate the remainder of the unoxidized ester from the hypophases.

The second stage formed the pattern for all subsequent stages and consisted of re-extracting each of the 100-ml. portions of the extractant in succession, beginning with the first, with a fresh 200-ml. portion of the Skellysolve F phase. At this point, after each of the 100-ml. portions of extractant were extracted in succession with the second epiphase, the solute in the epiphase consisted mostly of unoxidized ester, but it was necessary to make two and sometimes three more extractions with 100-ml. portions of fresh extractant to assure complete recovery of the peroxides. Essentially complete recovery of the peroxides was assured by the introduction of as many stages as were necessary.

Concentration of Peroxides. Tables II, III, and IV show the complete stage by stage concentration of the peroxides from autoxidized methyl linoleate, linolenate, and oleate, respectively.

TABLE II

Isolation of Peroxide Fraction of Autoxidized Methyl Linoleate (P. V. 990 m.e./kg.)

Stage	Plates	Epiphase			Hypophase		
		Total unoxidized ester separated	Unoxidized ester	Oxidized ester	Unoxidized ester	Oxidized ester	Concentration of peroxide in solute
		%	*g.*	*g.*	*g.*	*g.*	%
Original sample	.....	.....	17.078	3.30	.....	.....	.....
1	8	57.8	9.858	0.012	7.220	3.288	31.3
2	11	83.25	4.343	0.004	2.877	3.284	53.4
3	14	93.1	1.681	nil	1.196	3.284	73.2
4	17	96.4	0.673	nil	0.523	3.284	86.3
5	20	98.7	0.294	nil	0.230	3.284	93.6
6	23	99.3	0.120	nil	0.110	3.284	97.0
7	26	99.7	0.053	nil	0.057	3.284	98.4
8	29	99.8	0.027	nil	0.030	3.284	99.3
9	32	99.9	0.012	nil	0.018	3.284	99.6
Totals	180	99.9	17.061	0.016	0.018	3.284	99.6

On the basis of the peroxide value the original autoxidized methyl linoleate contained 3.3 g. of oxidized material (monoperoxidic) and 17.078 g. of unreacted ester. The progress of the separation is shown in Table II by the amount of material extracted into the epiphase after each successive stage. It is apparent that very little more material would be preferentially extracted into the epiphase by applying more than nine stages in this experiment. Thus the separation was considered essentially complete although an even finer separation might have been obtained by applying an additional plate in stage one. The total weight (17.221 g.) of material separated in the combined epiphases nevertheless was in excellent agreement with the amount of unoxidized water originally present as calculated from the peroxide value. The weight of material in the combined hypophases was 3.284 g., which was in excellent agreement with the calculated value of 3.3 g. of monoperoxidic material present in the original sample. The peroxide value of the material separated in the hypophase was 6,100 m.e./kg. This value and the results of other chemical determinations to be reported elsewhere (9) indicated that the product was essentially

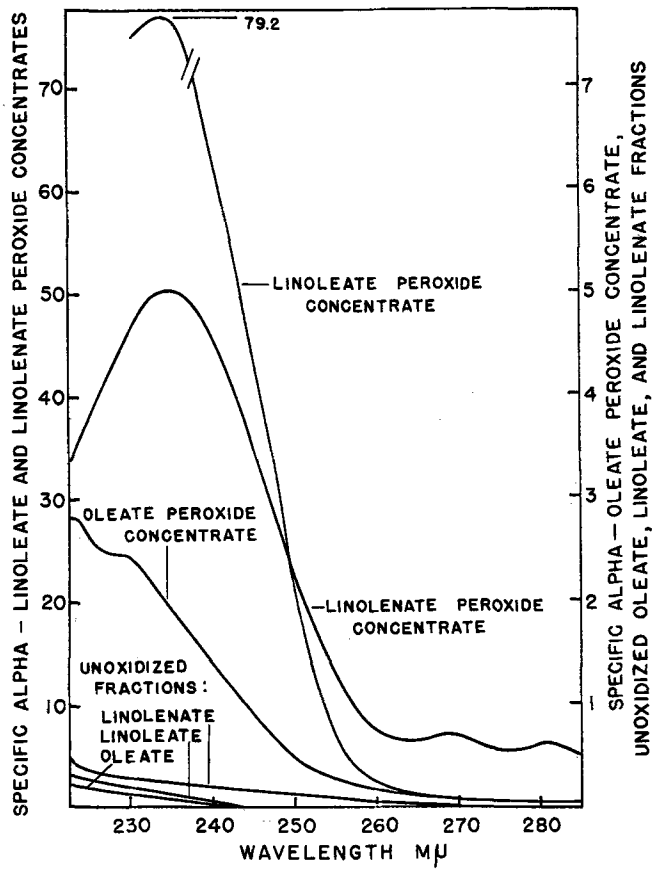

FIG. 1.

TABLE III

Isolation of the Peroxide Fraction of Autoxidized Methyl Linolenate (P. V. 760)

Stage	Plates	Epiphase			Hypophase		
		Total unoxidized ester separated	Unoxidized ester	Oxidized ester	Unoxidized ester	Oxidized ester	Concentration of peroxide in solute
		%	g.	g.	g.	g.	%
Original sample	.....	.....	73.69	10.480	0	0	.....
1	12	50.60	37.294	0.106	36.396	10.374	22.2
2	15	64.78	14.126	0.014	27.270	10.360	31.8
3	18	82.16	9.126	nil	13.144	10.360	44.1
4	21	90.12	5.877	nil	7.267	10.360	58.8
5	24	94.17	3.113	nil	4.154	10.360	71.4
6	27	96.54	1.747	nil	2.407	10.360	81.2
7	30	98.11	1.154	nil	1.253	10.360	89.2
8	33	99.04	0.685	nil	0.568	10.360	94.6
9	36	99.56	0.370	nil	0.198	10.360	98.2
10	39	99.87	0.234	nil	0	10.360	100.0
11	42	100.08	0.160	nil	0	10.360	100.0
Totals	297	100.08	73.886	0.120	0	10.360	100.0

pure monoperoxide. The completeness of the separation of the unoxidized and oxidized fractions was also indicated by the ultraviolet absorption spectra as shown in Figure 1. These spectra were obtained with a Beckman model DU spectrophotometer, using purified 95% ethyl alcohol as the solvent.

Table III shows that it required 11 stages and a total of 297 plates to separate the unoxidized from the oxidized fraction of autoxidized methyl linolenate. The materials in the combined epiphases were found to consist of almost pure unoxidized ester. The peroxide value of the material segregated in the combined hypophases was 6,000 m.e./kg. but, in contrast to the peroxides separated from autoxidized linoleate, the linolenate peroxide concentrate did not consist entirely of monoperoxides. Further fractionations, the complete results of which will be reported elsewhere (10), yielded some fractions with peroxide values as high as 8,000 m.e./kg. and other fractions with peroxide values considerably below the theoretical value of 6,125 for pure linolenate monoperoxide. It has not been determined whether the low peroxide values in some fractions were due to the presence of unoxidized linolenate or to the presence of oxidation products other than peroxides.

The ultraviolet absorption spectra of the unoxidized and oxidized fractions are given in Figure 1. The maximum specific absorption coefficient in the case of linolenate peroxides was 50.8 at 236 mμ.

TABLE IV

Isolation of the Peroxide Fraction of Autoxidized Methyl Oleate (P. V. 1670)

Stage	Plates	Epiphase			Hypophase		
		Total unoxidized ester separated	Unoxidized ester	Oxidized ester	Unoxidized ester	Oxidized ester	Concentration of peroxide in solute
		%	g.	g.	g.	g.	%
Original Plates	.....	.....	14.1784	5.4734	0	0	.....
1	12	41.90	5.9249	0.0211	8.2535	5.4523	39.80
2	15	68.00	3.7017	0.0157	4.5518	5.4366	54.50
3	18	81.80	1.9637	0.0126	2.5881	5.4240	67.80
4	21	89.00	1.0214	0.0080	1.5667	5.4099	77.50
5	24	93.00	0.5406	nil	1.0261	5.4019	84.10
6	27	94.50	0.2355	nil	0.7906	5.4019	87.50
7	30	95.60	0.1692	nil	0.6214	5.4019	90.00
8	33	93.30	0.0819	nil	0.5395	5.4019	91.20
9	36	96.50	0.0453	nil	0.4942	5.4019	92.00
10	36	97.00	0.0633	nil	0.4309	5.4019	92.60
Totals	252	97.00	13.7475	0.0715	0.4309	5.4019	92.60

In the case of autoxidized methyl oleate Table IV shows that although the separation of the unoxidized from the oxidized fraction was complete, there appeared to be less unoxidized material present than was indicated by the peroxide value. Further examination of the countercurrent extraction data revealed that the disparity between the calculated unoxidized material originally present and the amount of material present in the combined epiphase was 3%. When this disparity is calculated in terms of oxidized material, it amounts to 8% of the peroxide fraction. The peroxide value of the material in the combined hypophase fractions was only 5,500, confirming the presence of oxidized material other than peroxides in this material. Since the autoxidation of the original methyl oleate was carried out at 50°C., it was believed that decomposition and possibly secondary reactions probably occurred at this temperature and account for the disparity between the calculated and experimental values. The ultraviolet spectra of the two fractions are also shown in Figure 1 and illustrated again the completeness of the separation of the oxidized from the unoxidized fraction. The specific absorption coefficient of the oxidized fraction at 228 mμ is approximately 20 times that of the nonperoxidic material separated in the combined epiphases.

Discussion

It is evident that to obtain quantitative information about the types and amounts of the products produced in the autoxidation of fatty acid esters, complete separation of the entire oxidized fraction from unoxidized ester is desirable. The quantitative data on the isolation of the oxidized fraction in the three samples of autoxidized fatty acid esters in this report demonstrate the usefulness of the technique that has been described for such purposes.

The procedure as described appears to separate all of the oxygenated derivatives of autoxidation from the unoxidized esters. Whether the oxidized fraction consisted almost entirely of monohydroperoxides as in the autoxidized methyl linoleate or contained a large proportion of secondary reaction products as in the autoxidized methyl oleate and linolenate, it was all separated in the alcoholic phases.

Semi-automatic extraction equipment of the Craig type can also be employed for the separation of the oxidized and unoxidized fractions of autoxidized fatty esters, but their value is limited by their small capacities and the relatively low concentration of materials that must be used.

Summary

Details of a countercurrent extraction procedure for the quantitative separation of the oxidized and unoxidized fractions of autoxidized fatty acid esters is described.

The utility of the process is demonstrated by the quantitative separation of the oxidized from the unoxidized fractions of autoxidized methyl linoleate, linolenate, and oleate.

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Alternative Methods for Dehydrating Castor Oil[1]

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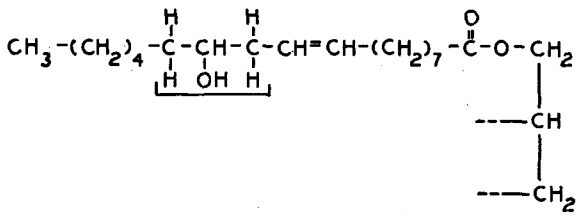
THE importance of dehydrated castor oil in coatings is shown by an annual consumption of some 30,000,000 lbs., which is about 5-6% of all drying oils used in coatings (8). Actually this oil is somewhat more important than the 5% figure indicates because its properties, which are intermediate to those of highly conjugated tung oil and non-conjugated linseed oil, make it especially valuable. Its use would undoubtedly increase if greater quantities were available at lower cost.

Castor oil is a unique non-drying oil in that it can be readily converted to a drying oil by the chemical reaction of dehydration:



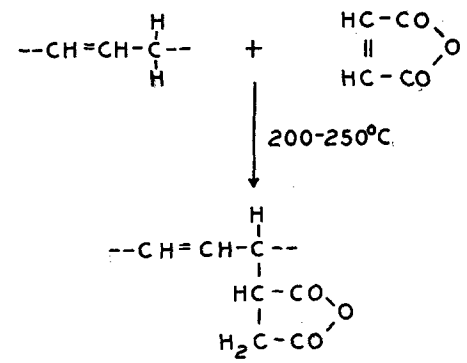
This transformation of the ricinoleic acid groups to isomeric octadecadienoic acid groups is analogous, in its simplest terms, to the formation of propylene from isopropyl alcohol.

From the extensive literature on dehydrating methods which consist of several hundred patents and journal articles (20), there appear to be four important considerations, in addition to the factor of processing cost: a) the dehydration reaction must be substantially complete to obtain an oil of good drying and film properties; b) the competitive reaction of polymerization or heat bodying must be controlled to avoid a viscous or even gelled product; c) catalysts for the dehydration must either be innocuous if left in the oil or readily removable; and d) an increase in the amount of two double bond conjugation over the 20-30% usually obtained would be desirable. With these factors in mind several new dehydration methods have been studied.

Dehydration by Oil-Maleic Adducts

The first of these dehydration methods is a variation of a method described earlier in which castor oil is heated with a quantity of phthalic anhydride insufficient to esterify all of the alcoholic hydroxyl groups (4). At the end of the reaction period there is free phthalic anhydride (or acid) which can be removed by filtration or esterified by a polyalcohol. Our development consists in the use of the addition compound from maleic anhydride and a non-conjugated oil, such as linseed or soya as the acid anhydride. The product then consists of dehydrated castor oil and a maleinized drying oil which need not be separated because it contributes valuably to film formation.

The reaction of maleic anhydride with non-conjugated oils at temperatures of about 200°C. is well known in the coatings industry (6). The most probable course of this reaction is as follows:



[1] Presented before the American Oil Chemists' Society, Houston, Tex., April 29, 1952.