

deodorization may prove to be a better indicator of fat deterioration than an AOM test made on the same oil as refined. Refined oils with AOM values over 8 hrs. showed lesser AOM values after deodorization and refined oils with AOM values under 8 hrs. showed higher AOM values after deodorization. A refined oil of zero AOM value had an AOM value of 5 hrs. after deodorization.

### Conclusions

There have been insignificant decreases in market value of seven out of eight drums of refined cottonseed oil held in storage for longer periods than are generally used in industry. Five drums containing oil from the same source (solvent-extracted and refined in miscella) had been held for 28 months under different types of storage. Three drums containing oil from different sources (screw-press and prepress-solvent extractions) had been held for 10 months under the same type of storage.

All of the oils entered storage as prime bleachable summer yellow, but one drum of oil became unbleachable after the first 10 months of storage. This oil however had a bleached color of 2.0 A.O.C.S. units originally, which was much higher than on the other oils.

There had been insignificant changes in free fatty acid, moisture and volatile matter, and refined color on all the oils.

Peroxide values have increased appreciably in some of the oils, and values of fat stability by the Active

Oxygen Method have decreased appreciably, especially on some of those oils stored for 28 months. However laboratory tests at the end of the storage periods do not indicate that a point of rancidity has been reached on any of the oils.

Although the flavor of all the oils was criticized quite extensively by most of the 46 members of industry who have cooperated in grading the oils, only about a quarter to a third of the graders would call the oils "off in flavor and odor" in accordance with Rules of the National Cottonseed Products Association. Furthermore only a few of these graders (from one to five in the cases of the several oils) would actually decrease the market value of the oil for being "off" in flavor, and this discount on the average was insignificant.

There were no relationships between the graders' judgments of the oils for "off flavor and odor" and the tests for peroxide value and AOM fat stability. Industry generally regards these tests as reliable indicators of quality. On the basis of these tests the oil in the drum only half-filled has shown the greatest deterioration at the end of the 28-month period whereas the oil in the drum having no breather has shown the least deterioration.

It must be emphasized that the information in this paper has been drawn from a small sample. Results from the larger number of test drums of oil now in storage may necessitate modifications in the conclusions reported.

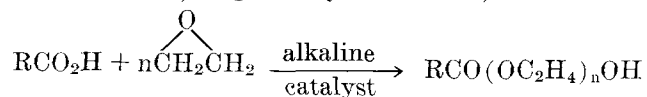
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## Reaction of Ethylene Oxide or Propylene Oxide with Long-Chain Fatty Acids. Mono- and Diester Formation<sup>1</sup>

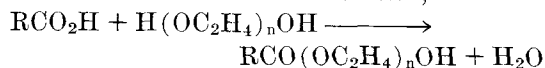
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**I**NEXPENSIVE fat-based nonionic detergents and surface-active agents are readily made by the reaction of ethylene oxide with long chain fatty acids, such as lauric or stearic acid, under the influence of an alkaline catalyst.

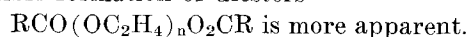
The reaction, as generally understood,



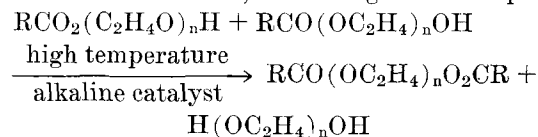
where  $\text{RCO}_2\text{H}$  is the parent fatty acid and  $n$  is the average number of ethenoxy groups, would lead only to the formation of monoesters (14). From this point of view the reaction with ethylene oxide would be preferred to the esterification reaction,



where the possible formation of diesters



There has been evidence in the case of acetic or benzoic acid (1, 15) that the reaction with ethylene oxide is more complex than is represented by the first equation. With respect to the higher fatty acids, transesterification (6) or alcoholysis may occur under the reaction conditions, according to the equation:



Furthermore a recently published method of analysis (7) has shown that water-soluble nonionic surface-active agents of the ester type, from the reaction of ethylene oxide with the higher fatty acids, are in reality composed of comparable amounts of glycols, monoesters, and diesters.

The monoester may be expected to be a more valuable detergent and surface-active agent than the diester, or than a mixture of monoester, diester, and polyethylene glycol. In any event the properties of a reasonably pure monoester preparation would be of interest. As an initial phase in understanding the

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TABLE I  
 Products Formed in the Alkenoxylation of Fatty Acids or Monoesters

Experiment No.	Acid or monoester	Cyclic ether	n	Reaction conditions	Analysis, mole % (7)			Molar ratio, mono-diester
					Glycols	Monoester	Diester	
1.....	Lauric acid	Ethylene oxide	1.03	a	14	36	50	0.72
2.....	Lauric acid	Ethylene oxide	1.03	b	18	44	38	1.15
3.....	Stearic acid	Ethylene oxide	1.08	a	24	34	42	0.81
4.....	Stearic acid	Ethylene oxide	1.19	c	....	....	....	1.21 <sup>d</sup>
5.....	Oleic acid	Ethylene oxide	0.69	b	14 <sup>e</sup>	68 <sup>e</sup>	17 <sup>e</sup>	3.90
6.....	Oleic acid	Ethylene oxide	0.94	b	41	32	27	1.20
7.....	Oleic acid	Ethylene oxide	12.1	b	31	45	24	1.85
8.....	Oleic acid	Ethylene oxide	16.3	b	31	42	26	1.61
9.....	Glycol monolaurate	Ethylene oxide	13.9	f	31	44	25	1.75
10.....	Lauric acid	1,2-Propylene oxide	1.00	b	26	40	34	1.18
11.....	Stearic acid	1,2-Propylene oxide	1.10	b	25	37	38	0.96

<sup>a</sup> Temperature 180–90°, 0.5% KOH catalyst, magnetic stirrer.

<sup>b</sup> 155–65°, 1% KOH, agitation by magnetic stirrer and gas-dispersion tube.

<sup>c</sup> Smaller scale experiment in graduated tube, 3 hrs. at 160°, 10 mole % 2-methylquinoline catalyst, agitation by gas-dispersion tube.

<sup>d</sup> From analysis of the crude crystalline solid precipitated from acetone at 0°.

<sup>e</sup> Unreacted oleic acid present; analysis based on oleic acid converted.

<sup>f</sup> Smaller scale experiment in graduated tube, 160°, 1% KOH, agitation by gas-dispersion tube.

reaction and the conditions which promote monoester formation, the present report concerns the alkali-catalyzed reaction of ethylene oxide or propylene oxide with lauric, stearic, and oleic acids, under conditions such that only about one mole of the oxide was condensed with one mole of the fatty acid.

The experiments centered around a low degree of ethenoxylation or propenoxylation because it was of interest to learn if transesterification, or alcoholysis, occurred to a significant extent even in the very early stages of the formation of detergents or surface-active agents. The low average value of *n* limited the average molecular weight and the number of homologous mono- and diesters formed. Thus it was possible to isolate chemical individuals by fractional distillation at low pressure in the lauric acid experiments, and by fractional crystallization from acetone in the stearic acid experiments.

#### Ratio of Mono- to Diester

In general, the reaction conditions were quite similar to those described previously (17). An agitated mixture of fatty acid and 0.5–1.0% KOH catalyst was heated in a stream of nitrogen to remove moisture. Ethylene oxide or propylene oxide was then introduced at a reaction temperature of 155–190° until the weight increase corresponded with the selected value of *n* (usually *n* = 1). A calculated amount of concentrated HCl was added to neutralize the catalyst, and the mixture was filtered and analyzed by the method of Malkemus and Swan (7) to determine the proportion of monoester, diester, and glycols (Table I).

Most of the experiments were carried out in 3-neck flasks charged with 150 g. or more of the fatty acid. A combination of conditions including a lower reaction temperature, an increased amount of catalyst, and more effective agitation (reaction conditions "b") somewhat encouraged monoester formation. The smaller scale experiments 4 and 9 were carried out in graduated tubes of 100 ml. and 50 ml., respectively. Catalysis with 2-methylquinoline (experiment 4), an amine unreactive with cyclic ethers (10), gave

results similar to those with the usual catalyst except that the reaction did not appear to proceed farther after one equivalent of ethylene oxide had been condensed.

Diester and glycol formation occurred even at a very early stage of ethenoxylation or propenoxylation. The ratio of mono- to diester was highest in the initial stage before complete conversion of the carboxylic acid (experiment 5), after which the ratio decreased or remained of the same order of magnitude with increasing values of *n*. Glycol monolaurate (experiment 9) also gave rise to polyethylene glycols and diesters with increasing ethenoxylation. A like experiment with glycol dilaurate showed no reaction: the diester was recovered unchanged. This failure to react is not unexpected but may be influenced by inadequate solubility of the catalyst.

#### Isolation of Individual Esters

*Lauric Acid Experiments.* After neutralization of the catalyst and removal of KCl by filtration, 300 g. of the lauric acid-ethylene oxide reaction product (experiment 1, Table I) were carefully distilled at reduced pressure, using an 18-in. Vigreux column. The course of distillation was followed by refractive index, melting point, and analyses for free fatty acid (as % lauric acid), saponification equivalent, and % hydroxyl. The fractions listed were selected and subjected to repeated crystallization from acetone at 0° or –25°.

In this manner ethylene glycol monolaurate, dilaurate, and diethylene glycol dilaurate were isolated in a pure state. Similar distillation of the lauric acid-propylene oxide reaction product led to the isolation of 1,2-propylene glycol dilaurate. The propylene glycol monolaurate was found to be a mixture of isomeric monoesters, as will be shown later.

*Stearic Acid Experiments.* The products from the stearic acid experiments could not easily be distilled. Ethylene glycol distearate and 1,2-propylene glycol distearate were isolated by repeated crystallization from acetone, a solvent in which the monoesters are more readily soluble.

Fraction	Grams	n <sub>D</sub> <sup>20</sup>	m.p.	% Lauric acid	S.E.	% OH	Distillation range/mm.
C-D.....	46	1.4327	22°	5.8	284	7.8	104–14°/0.005
H-K.....	80	1.4350	48–50°	0.2	219	0.3	186–90°/0.02
N.....	21	1.4360	42–45°	0.3	231	0.1	197–201°/0.04

TABLE II  
 Isolated Mono- and Diesters

Experiment No.	Ester	Boiling point <sup>c</sup>	Melting point or freezing point	$n_D^{20}$
1.....	$C_{11}H_{23}CO_2C_2H_4OH$ , ethylene glycol monolaurate	114°/0.005	31.6–32.0°	1.4330, $t=60^\circ$
2.....	$(C_{11}H_{23}CO_2CH_2)_2$ , ethylene glycol dilaurate	188°/0.025	51.6–52.1°	1.4348, $t=60^\circ$
3.....	$(C_{11}H_{23}CO_2CH_2CH_2)_2O$ , diethylene glycol dilaurate <sup>a</sup>	200°/0.04	38.8–39.7°	1.4360, $t=60^\circ$
4.....	$(C_{17}H_{35}CO_2CH_2)_2$ , ethylene glycol distearate	.....	74.4–75.0°	1.4369, $t=75^\circ$
5.....	$C_{11}H_{23}CO_2CH_2CHOHCH_3$ , $C_{11}H_{23}CO_2CH(CH_3)CH_2OH$ , 1,2-propylene glycol monolaurate <sup>b</sup>	126°/0.005	6–6.5° (f.p.)	1.4417, $t=30^\circ$
6.....	$C_{11}H_{23}CO_2CH_2CH(CH_3)O_2CC_{11}H_{23}$ , 1,2-propylene glycol dilaurate <sup>a</sup>	196°/0.04	21.9° (f.p.)	1.4443, $t=30^\circ$
7.....	$C_{17}H_{35}CO_2CH_2CH(CH_3)O_2CC_{17}H_{35}$ , 1,2-propylene glycol distearate	.....	58.2–59.0°	1.4412, $t=60^\circ$

<sup>a</sup> New compounds. Analyses: Calcd. for  $C_{28}H_{54}O_5$ , 71.44% C, 11.56% H; found 71.62, 11.43. Calcd. for  $C_{27}H_{52}O_4$ , 73.58% C, 11.89% H; found 73.62, 11.92.

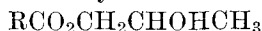
<sup>b</sup> Found by chromic acid oxidation to be a mixture of the 1- and 2-monolaurate.

<sup>c</sup> Distillation temperature of the principal fraction at the indicated pressure in mm.

**Analysis and Physical Constants.** Analyses for carbon and hydrogen, saponification equivalent, and percentage of hydroxyl agreed with the calculated values for all the compounds of Table II. The melting points are also in agreement with those values which can be found in the literature (8, 13, 16) except that an unusually high melting point of 72.3° has been reported for 1,2-propylene glycol distearate (5). The density,  $d_4^{30}$ , was found to be 0.9133 for propylene glycol monolaurate, and 0.8972 for propylene glycol dilaurate. Experimental molecular refractivity values checked with the sum of atomic refractivities.

### Propylene Glycol Monolaurate

Not much information exists in the literature concerning the relative amounts of isomeric monoesters to be expected in the alkali-catalyzed reaction of propylene oxide with fatty acids. Chitwood and Freure (2) have shown that the product with lower alcohols is almost exclusively the secondary alcohol  $ROCH_2CHOHCH_3$ ; Fraenkel-Conrat and Olecott (4) obtained only secondary alcohol esters



from the reaction with butyric or valeric acids under conditions such that only monoesters were formed; and Ross (12) showed that reaction with benzoate ion gave both the 1- and the 2-monobenzoate. However none of these reaction conditions quite coincided with those of our experiments.

The method used to show the presence of the two monolaurates (No. 5, Table II) was based on oxidation, and on separation and identification of the resulting keto ester and carboxylic acid ester.

Oxidation of the propylene glycol monolaurate with chromic acid in acetic acid gave an acidic oil, which gave a positive test for an  $\alpha$ -keto with triphenyltetrazolium chloride. The acidic portion was separated by salt formation with 2-aminopyridine (11) in ligroin and was isolated as the 2-aminopyridine salt of O-lauroylactic acid m.p. 82.8–83.4° (analysis: calculated for  $C_{20}H_{34}N_2O_4$ , 65.54% C, 9.35% H, 7.64% N; found 65.74, 9.76, 7.53, respectively). O-Lauroylactic acid m.p. 34.8–35.6° was regenerated from the salt and converted to lactanilide laurate m.p. 107.8–108.4° [no m.p. depression with an authentic sample (3)]. The identity of the ester acid from oxidation was further confirmed by comparison with O-lauroylactic acid m.p. 36.0–36.5° synthesized from lauroyl-lactamide (3) by the action of nitrosyl chloride. The two samples of O-lauroylactic acid showed no significant depression of the melting point on mixing and had the same characteristic infrared absorption.

Repeated crystallization of the nonacidic portion from acetone gave acetonyl laurate m.p. 30.7–31.0°, converted to the 2,4-dinitrophenylhydrazone m.p. 78.5–79.0°. These melting points are in good agreement with those in the literature (9).

Examination of the oxidation product showed that the ratio 1-monolaurate:2-monolaurate was approximately 2:1, but the alternative types of propylene oxide ring opening did not necessarily occur in this ratio because of the possibility of forming either isomeric monoester from the dilaurate by alcoholysis.

### Summary

The alkali-catalyzed reaction of ethylene oxide or propylene oxide with fatty acids was shown to be complex. Mono- and diesters were formed in comparable amounts even at an early stage when only about one equivalent of the cyclic ether had been condensed.

The following compounds were isolated in a pure state: ethylene glycol monolaurate, ethylene glycol dilaurate, diethylene glycol dilaurate, ethylene glycol distearate, 1,2-propylene glycol dilaurate, and 1,2-propylene glycol distearate. A monoester from propylene oxide was shown to be a mixture of the 1- and 2-monolaurate [ $C_{11}H_{23}CO_2CH_2CHOHCH_3$  and  $C_{11}H_{23}CO_2CH(CH_3)CH_2OH$ ].

### Acknowledgment

Microanalyses for C, H, and N were performed by Miss Laverne Scroggins.

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