heat of formation of acids was greater than that of the corresponding esters.

A comparison of yields from ethyl *n*-caprate and *n*-hexyl-*n*-caproate, which differ only in the relative position of the ester group along the carbon chain, was made (Table II). Moving the polar group from near the end of the molecule to its center decreased the yield. The improved tendency of esters to yield inclusion compounds thus is not due to shifting the polar group of the acid away from the end of the molecule.

The presence of double bonds in the fatty acid molecules introduces steric irregularities in the fatty acid chain and consequent imbalance of the optimum intermolecular distances, diminishing the net attractive force stabilizing the inclusion compound. Shortening the carbon chain also reduces the energy of inclusion compound formation. With long chain saturated compounds the energy of formation of urea inclusion compounds is high and differences between acids and their esters are not apparent, but when the chain length is shortened or made irregular by the presence of double bonds, the total energy of formation is reduced to a point where differences between acid and ester are significant. It may be that the hydrogen bonding of two acids in an associated dimer reduces the total energy available for urea inclusion compound formation but that the potential ability of the carbonyl group to hydrogen bond with urea in the crystal lattice remains in the ester.

Summary

1. Urea segregation has been found to be a useful tool in concentration of highly unsaturated acids and esters. Fatty acids and esters derived from fish oils and methyl esters of hog adrenal fatty acids have been fractionated, and the polyunsaturated acids have been enriched.

2. The tendency for fatty acids and esters to combine with urea decreases with increasing unsaturation. Combination is favored by lowered temperature. Polyunsaturated acids are concentrated in the final filtrate whereas esters of these acids appear in the final inclusion compound fractions. Fatty acid concentrates have been obtained with iodine values ranging from 294 to 356. Bound esters exhibited iodine values as high as 338.

3. The increased chain length brought about by esterification has a minor role in increasing the yield of inclusion compounds. Likewise, shifting of the terminal polar group in an acid toward the center of the molecule by esterification does not explain the higher yield of inclusion compound from esters.

4. The improved tendency of esterified acids to form urea inclusion compounds is probably due to blocking of association of acid groups. This effect is found in unsaturated acids and in short chain saturated acids. In long chain saturated acids and esters this effect is not noticed. Both give high yields of inclusion compounds because the effect of the carboxyl group is overshadowed by the high energy of formation contributed by the long carbon chain.

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Comparative Detergency of Several Built Polyethenoxy Alkanoates

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NONIONIC detergents are generally composed of a hydrophobic radical such as a fatty or rosin acid (RCOOH) solubilized by a hydrophilic end group such as a polyethenoxy chain:

$$R\text{-}COO\text{-}(CH_2\text{-}CH_2\text{-}O)_x\text{-}H$$

In a previous article (1) the comparative detergency of polyethenoxy tallates was presented, and the optimum polyethenoxy or hydrophilic chain length for various tall oils rich in mixtures of fatty as well as rosin acids was determined. It seemed desirable to investigate the effect on detergency of the hydrophobic or alkanoate chain length in nonionic esters as well as the optimum ethenoxy chain length for each fatty acid. Therefore pelargonic, lauric, myristic, and stearic acids were condensed with various proportions of ethylene oxide, and the average molecular size of each sample was accurately determined by a saponification equivalent. Comparative detergency values in hard and soft water were determined on built compositions of each condensate, and the optimum combinations of hydrophobic to hydrophilic chain lengths were ascertained.

Since tall oils are known to contain secondary alcohols, such as various sterols in the non-saponifiable fraction along with the rosin and fatty acids, it became of interest to study the condensation of an alkanoic acid containing a secondary hydroxyl group and to ascertain the relative proportions of ether to ester formation as well as to determine the effect, if any, upon detergency. Since primary long chain alcohols have been successfully condensed (2) with ethylene oxide in the presence of caustic soda, it was naturally assumed that the condensation product of the readily obtainable 12-hydroxystearic acid with ethylene oxide would contain ethenoxy groups in ether as well as ester linkage. The molecular size of each sample was determined from a saponification equivalent, and the number of etherified ethenoxy groups was obtained by performing a neutral equivalent on the saponified acids with the remaining ethenoxy groups assumed to be in ester formation. In addition, comparative detergency values in hard and soft water were determined for the nonionic esters from 12-hydroxystearic acid, and the results are presented herein.

Preparation of Polyethenoxy Esters

The alkanoic acid (100 g.) was admixed with 0.5 g. of potassium carbonate in a tared three-neck flask with a gas disperser inlet, thermometer, and outlet tube. The mixture was heated in an atmosphere of nitrogen gas to 160°C., and ethylene oxide gas was added at such a rate as to maintain the temperature between 160-190°C. The amount of absorbed gas was determined by weighing the entire apparatus periodically, and at various intervals a sample of polyethenoxy ester was removed and analyzed for its ethenoxy content by a saponification equivalent (3). Table I indicates the composition and water solubility of various nonionic esters prepared in the above manner. Detergency values, *i.e.*, soil removal and whiteness retention in hard (252 ppm as $CaCO_3$) and soft water, were determined by the method described by Vaughn and Suter (4) with slight modification (1). Test mixtures were prepared, using 20% by weight of polyethenoxy alkanoate, 20% tetrasodium pyrophosphate, 20% sodium tripolyphosphate, 39% soda ash, and 1% carboxymethylcellulose. Detergency values were compared to the previously described (1) arbitrary standard test mixture taken as 100%. The standard contained nonionic detergent and alkaline builders similar to those described above. In all cases 0.25 g. of test mixture per 100 ml. of solution was used for the detergency measurements.

TABLE I

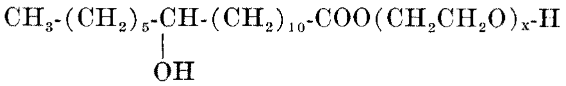
Composition of Polyethenoxy Alkanoates

	No. Ethenoxy Groups		Clear Solution [a] in Water
	By Weight	By Saponification Equivalent	
Polyethenoxy Pelargonate	2	1.8	—
	4	4.0	—
	6	6.3	—
	8	8.0	±
	10	9.8	+
Polyethenoxy Laurate	4	4.0	—
	6	6.3	—
	8	8.3	±
	10	11.6	+
Polyethenoxy Myristate	6	5.9	—
	8	7.45	±
	10	9.15	+
	12	11.6	+
	14	14.4	+
Polyethenoxy Stearate	8	8.08	—
	10	10.7	—
	12	12.6	—
	14	14.8	—
	16	16.5	—
	20	23.9	+
Polyethenoxy 12-Hydroxystearate (K_2CO_3)	6	5.9	—
	8	8.1	—
	10	10.2	±
	12	12.7	+
	14	15.6	+
Polyethenoxy 12-Hydroxystearate (KOH)	12	12.5	+
	14	15.2	+
	25	23.0	+
	40	39.0	+

[a] Room Temp., 0.25% Solution. (+) Clear, (—) Cloudy, (±) Borderline.

The condensation of 12-hydroxystearic acid with ethylene oxide and potassium carbonate was carried out in the above-described manner, and the acid was recovered from each saponified ester. A neutral equivalent and melting point were determined on each sample. The acid from the 12-hydroxystearate containing 15.6 ethenoxy groups was shown to be the original starting material, namely 12-hydroxystearic acid by melting point, 77-79°, mixed melting point with an authentic sample, 77-78°, and by its neutralization equivalent, theor. 300; obtained 291. Similar results were obtained with the acids obtained from the polyethenoxy 12-hydroxystearates containing fewer ethenoxy groups (see Table I). Since these results indicated that condensation of 12-hydroxystearic acid with ethylene oxide in the presence of potassium carbonate resulted in polyethenoxy ester formation with the exclusion of any ether formation on the secondary hydroxyl group of the acid, the above condensation was repeated with 12-hydroxystearic acid and ethylene oxide but in the presence of potassium hydroxide.

It had been noted in several experiments that secondary fatty alcohols, which did not condense with ethylene oxide in the presence of potassium carbonate, did so by use of the more basic potassium hydroxide. The potassium hydroxide catalyzed condensation product with 12-hydroxystearic acid containing 12.5 ethenoxy units was saponified, and a melting point (77-78°) and neutral equivalent (314) on the recovered acid indicated it also to be the original 12-hydroxystearic acid. This is further substantiated by comparing detergency values of the hydroxide and carbonate catalyzed reaction products. As a further check, the KOH catalyzed polyethenoxy 12-hydroxystearate was condensed with ethylene oxide until 23 and 39 ethenoxy units had been condensed, respectively. Upon saponification of these esters the hydroxystearic acids were separated and gave neutral equivalents of 317 and 324, respectively; their melting points indicated that both products were essentially 12-hydroxystearic acid. Thus it appears that the character of the condensation product of ethylene oxide with 12-hydroxystearic acid is not affected by the type of catalyst used in its preparation, and the polyethenoxy 12-hydroxystearate so obtained either with KOH or K_2CO_3 catalyst may be represented by the following formula:



$$CH_3\text{-}(CH_2)_5\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}(CH_2)_{10}\text{-}COO(CH_2CH_2O)_x\text{-}H$$

It could be inferred that under these experimental conditions the substances containing secondary alcoholic groups in tall oil, such as the sterols, do not condense with ethylene oxide in the presence of tall oil fatty acids and hence are present as water-insoluble impurities in the nonionic detergent polyethenoxy tallates.

The comparative detergency values, namely soil removal and whiteness retention of the polyethenoxy esters in hard water and soft water, are graphically presented in Figures 1 through 4 as a function of ethenoxy chain length. Figure 5 represents maximum soil removal and whiteness retention values in hard and soft water as a function of the hydrocarbon chain length.

Effect of Ethenoxy Chain Length Upon Detergency

From Figures 1 through 4 it becomes apparent that the detergency increases with increasing ethenoxy chain length but levels off at a maximum value, as has been noted previously (1) with the polyethenoxy tallates. The optimum detergency may be designated as that point at which the detergency begins to level off. It was then noted that this point varied with the chain length or molecular weight of each fatty acid and that additional ethenoxy units were needed to solubilize the longer chain acids.

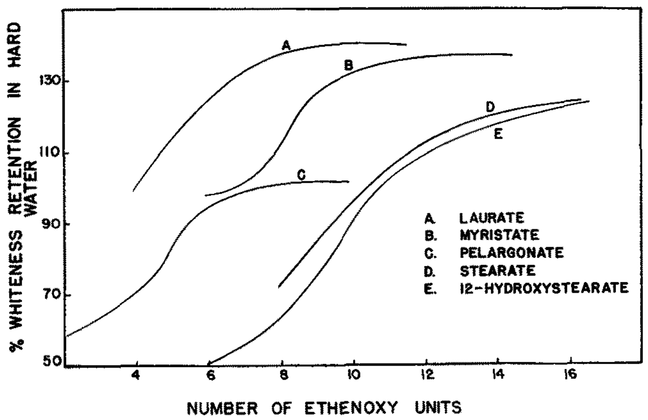


FIG. 1. Variation in whiteness retention in hard water of polyethenoxy alkanoates with ethenoxy chain length.

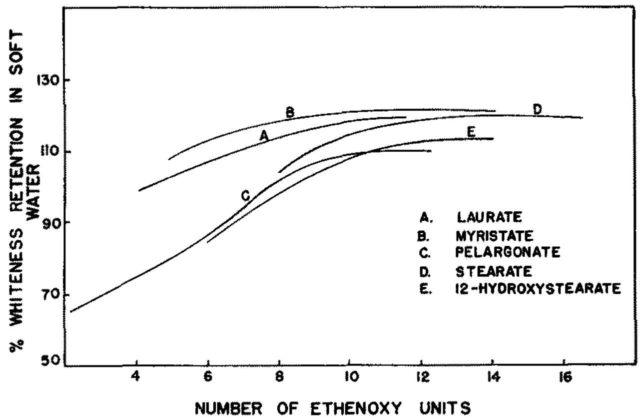


FIG. 2. Variation in whiteness retention in soft water of polyethenoxy alkanoates with ethenoxy chain length.

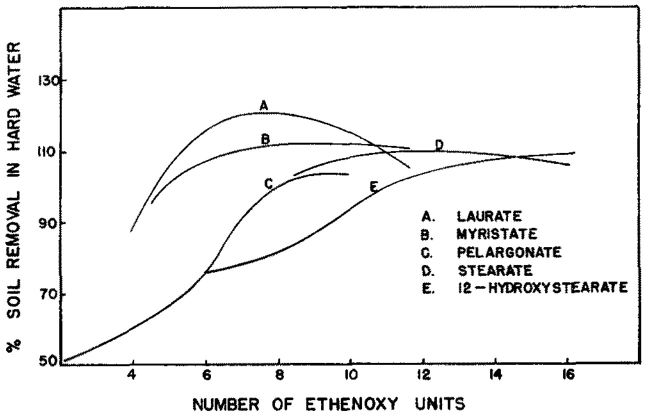


FIG. 3. Variation in soil removal in hard water of polyethenoxy alkanoates with ethenoxy chain length.

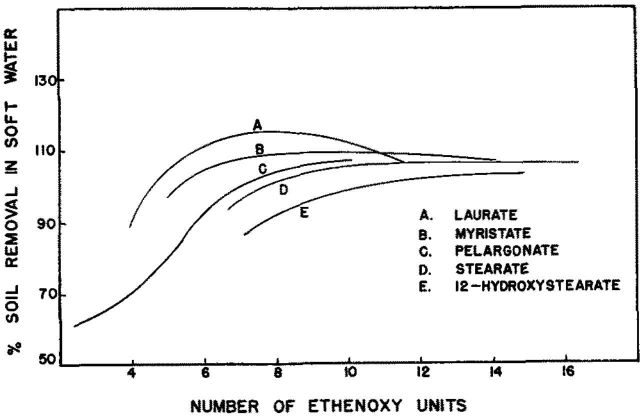


FIG. 4. Variation in soil removal in soft water of polyethenoxy alkanoates with ethenoxy chain length.

In general, approximately two-thirds of one ethenoxy unit is required for optimum detergency for each carbon atom in the fatty acid chain. This rule holds equally well for the polyethenoxy tallates (1) and should provide an empirical method for determining the quantity of ethylene oxide required by any fatty acid or mixture of fatty acids to produce a nonionic ester of optimum detergency. It is interesting that this is also the point at which the polyethenoxy esters assume water solubility. Actually it should be pointed out that not all of the ethylene oxide is present as polyethenoxy alkanoate since upon vacuum distillation of one of the polyethenoxy tallates there were obtained low boiling alcohols, probably ethylene glycol and diethylene glycol. Likewise it should be mentioned that not all of ethenoxy units in a given ester are of the same number but that a distribution curve similar to the one given for polyethylene glycols by Flory (5) probably applies in this case. Therefore the so-called optimum detergency values probably represent a larger quantity of ethylene oxide than should be required in the absence of glycol formation.

Effect of Fatty Acid Composition

From Figure 5 it will be noted that the chain length of the fatty acid or hydrophobic portion of the nonionic ester certainly affects overall detergency. The nonionic esters prepared from lauric and myristic acids show greater maximum detergency values, particularly in hard water, over the esters prepared from pelargonic, stearic, and 12-hydroxystearic acids. It should also be pointed out that the polyethenoxy laurates show decreasing soil removal values with prolonged ethenoxy chain length. This effect is not shown with some of the other acids. For example, a polyethenoxy stearate with 23.9 ethenoxy units was prepared and showed no loss in detergent potency.

Another effect worth noting is the slightly lower detergency values obtained for the polyethenoxy 12-hydroxystearates in comparison to the stearates. The presence of an unsubstituted secondary hydroxyl group apparently detracts slightly from the detergency of nonionic esters.

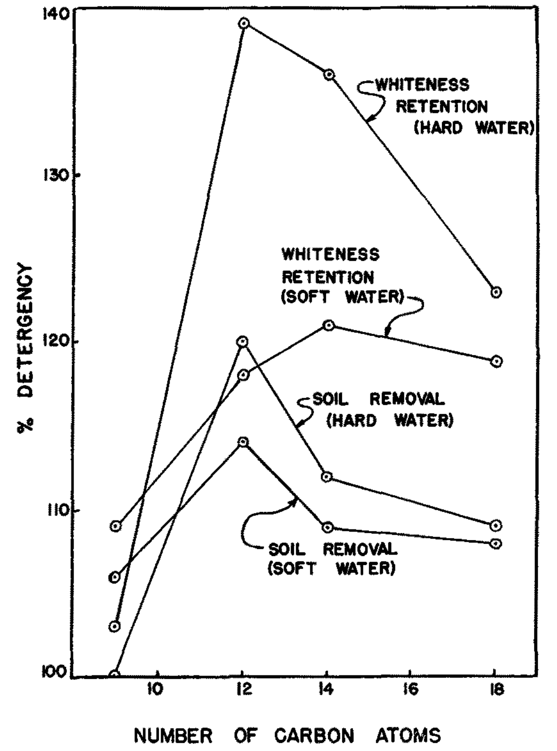
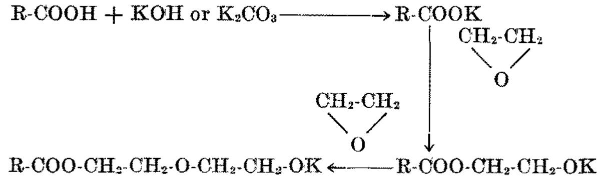


Fig. 5. Variation in detergency with number of carbon atoms in the fatty acid chain.

Remarks on the Mechanism of Ethenoxification

The esterification followed by etherification with ethylene oxide, more conveniently termed herein as "ethenoxification," apparently proceeds on the hydroxyl group of greatest acidity. This statement is based on the inability to etherify the secondary hydroxyl group of 12-hydroxystearic acid in the presence of the carboxyl group or primary alcohol group. It is well known that ethenoxification proceeds only in the presence of an alkaline catalyst. The reaction probably proceeds in the following manner wherein the catalyst actually enters into the reaction.



$$\begin{tikzcd} R\text{-}COOH + KOH \text{ or } K_2CO_3 \arrow[r] & R\text{-}COOK \arrow[d, "\underset{O}{CH_2\text{-}CH_2}"] \\ R\text{-}COO\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OK & R\text{-}COO\text{-}CH_2\text{-}CH_2\text{-}OK \arrow[l, "\underset{O}{CH_2\text{-}CH_2}"'] \end{tikzcd}$$

Since the primary alcoholic group in monoethenoxy 12-hydroxystearate is more acidic than the secondary hydroxyl group, the ethenoxy groups apparently add directly to the potassium salt of the primary alcohol exclusively. There is also some evidence that the carboxyl group is completely esterified before any primary alcoholic hydrogens are replaced. For example, titratable acidity of a monoethenoxy pelargonate was found to be negligible. It is also interesting that the addition of the first ethenoxy group to the carboxyl group proceeds at a substantially slower rate than subsequent ethenoxification.

Summary

Polyethenoxy alkanoates of varying ethenoxy chain length were prepared, and comparative detergency values were obtained on these substances. It was noted that approximately two-thirds of one ethenoxy group for each carbon atom in the hydrophobic portion of the molecule was essential for optimum detergency values. The nonionic esters prepared from lauric and myristic acids possessed substantially greater detergency than pelgargonic and stearic acids. 12-Hydroxystearic acid was likewise condensed with ethylene oxide, and curiously enough no ethenoxy groups were found attached to the secondary hydroxyl group. A partial explanation for this behavior based on the addition of ethylene oxide to the hydroxyl group of greatest acidity is presented.

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Evidence for Hydroperoxide Formation in the Autoxidation of Methyl Linolenate[1,2]

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The course and mechanism of the autoxidation of nonconjugated polyene fatty acid esters are considered by some investigators to have the same general pattern (1, 3). Hydroperoxides are considered to be the primary initial reaction products; other reactions that occur such as polymerization, formation of diperoxides and cylic peroxides and scission, are believed to follow to an extent determined by such factors as time, temperature, surface area, etc. The autoxidation of oleates is also believed to follow the same general pattern except that cyclic peroxides as well as hydroperoxides are believed to be produced in the early stages of the reaction, at least under some conditions (12).

Fugger *et al.* (5) in a recent study on the autoxidation of methyl linolenate however proposed that the course of the autoxidation of this ester is significantly different from that of methyl oleate and methyl linole-

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[2] Hormel Institute publication no. 95 and paper no. 157 Journal Series, General Mills Research Laboratories.

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