being less resistant in this respect than the acetostearins. These molded specimens were originally an opaque white or light cream color, as were all the molded sheets plasticized with acetoglycerides. It may be postulated that any development of odors by oxidative rancidity may be arrested by the use of antioxidants.

The overall results of the screening tests suggest the following generalities:

1. Unsaturation seems to effect improvement in efficiency and brittle point.
2. Mono-unsaturation tends to increase the compatibility but, as shown by aceto-oleins C and D, the presence of di-unsaturation (linoleic acid radical) tends to nullify this effect. This is partially confirmed by the better compatibility exhibited by the 50-50 blends of DOP with aceto-stearins than by a similar blend with aceto-olein C.
3. A higher degree of acetylation, as exemplified by the aceto-stearins, also tends to improve compatibility.

## Summary

The screening evaluation experiments on a number of acetoglycerides have indicated that they can be used as secondary plasticizers to improve some of the plasticizing qualities of plasticizers, such as tricresyl phosphate and Santicizer 141, and as extenders for plasticizers, such as dioctyl sebacate. Additional information will be necessary in order to confirm the tentative conclusions drawn as to the effect of unsaturation, polyunsaturation, and degree of acetylation upon the plasticizing characteristics of the acetoglycerides to determine more precisely their potentialities for vinyl chloride resins and to extend the possible use of the acetoglycerides as plasticizers to other resins.

## Acknowledgment

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# Tall Oil Studies. I. Effect of Chain Length and Composition on Detergency of Built Polyethenoxy Tallates

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A COMPREHENSIVE study of the condensation of ethylene oxide with a variety of fatty acids, alcohols, and amines to form the respective non-ionic, detergent polyethenoxy derivatives (polyoxyethyleneglycol esters) was carried out by Schoeller and Wittwer (1) in 1934. More recently Harris and Kosmin (2, 3) described non-ionic detergent compositions containing ethylene oxide condensation products of tall oil, a by-product of the pine-wood paper industry. The major constituents of this oil consist of approximately seven rosin acids related to abietic acid and three fatty acids related to oleic acid (4). The proportions of rosin acids to fatty acids may vary with the source and grade as well as the processing of the tall oil. Representing the tall oil acids by the conventional formula R-COOH, the corresponding non-ionic detergent esters with ethylene oxide, polyethenoxy tallates, may be written as follows:

$$\text{R-C-O-O(CH}_2\text{-CH}_2\text{-O)}_x\text{-CH}_2\text{-CH}_2\text{-OH}$$

It seemed desirable to study the effect of composition of tall oil as well as the polyethenoxy chain length upon detergency. With that in mind various grades and compositions of tall oil were condensed with ethylene oxide, and soil removal and whiteness retention assays were determined on the resultant polyethenoxy tallates in alkaline-built detergent compositions. In like manner two tall oil samples, one rich in rosin acid and the other rich in fatty acid, were condensed with ethylene oxide progressively, and detergency values were obtained on built compositions of the polyethenoxy tallates of varying ethenoxy chain length. As a check on the number of ethenoxy groups in the various esters a saponification method was applied to these substances, and details are described herein.

## Detergency Tests

The procedure used for evaluating detergency, *i.e.*, soil removal and whiteness retention in hard and soft water, of the various polyethenoxy tallates was essentially the method described by Vaughn and Suter (5) except that the swatches in the whiteness retention tests were dried in an oven at 110°C. for 30 minutes, with subsequent hand-ironing. Test mixtures were prepared, using 20% by weight of the polyethenoxy tallate, 20% tetrasodium pyrophosphate, 20% sodium tripolyphosphate, 39% soda ash, and 1% carboxymethyl cellulose. All results are comparative, *i.e.*, based on an arbitrary standard. For this purpose a commercially available similar, non-ionic built detergent mixture was chosen, and detergency of the test solutions containing 0.25% (0.25 g. test mixture/100 ml. water) of the standard was taken as 100% (see Table I). Detergency of the test solutions of the unknown were also determined at 0.25% concentration.

## Effect of Tall Oil Composition on Detergency

Six polyethenoxy tallates were prepared by condensing tall oils, varying in composition from pure abietic acid to pure oleic acid, with ethylene oxide gas in an inert atmosphere at 170-190°C., using potassium carbonate as a catalyst. In each case approximately 14 ethenoxy units were added to the carboxyl group. Detergency values of the products are compared in Table I.

TABLE I
Detergencies of Various Polyethenoxy Tallates

| Polyethenoxy tallate ratio | | Detergency | | | |
|---|---|---|---|---|---|
| | | Soil removal | | Whiteness retention | |
| Rosin acid | Fatty acid | Hard water | Soft water | Hard water | Soft water |
| | | % | % | % | % |
| Non-ionic detergent mix[a] | | 100 | 100 | 100 | 100 |
| 0 | 100[b] | 112 | 109 | 108 | 121 |
| 10 | 90 | 99 | 112 | 121 | 127 |
| 30 | 70 | 119 | 116 | 117 | 122 |
| 45 | 55 | 120 | 144 | 127 | 129 |
| 55 | 45 | 124 | 129 | 125 | 125 |
| 90 | 10 | 110 | 122 | 115 | 116 |
| 100[c] | 0 | 132 | 127 | 119 | 125 |

[a] Commercially available; [b] oleic acid; [c] abietic acid.

From the results in Table I it would appear that polyethenoxy tallates prepared from tall oils containing a larger proportion of rosin acid have slightly improved overall detergency. However difference in composition does not appear to be a significant factor.

### Effect of Polyethenoxy Chain Length Upon Detergency

For this experiment two tall oils, A and B, were selected. The former had a rosin acid/fatty acid ratio of 30/70, and the latter contained 90 parts of rosin acid to 10 parts of fatty acid. Each sample of tall oil was condensed with ethylene oxide gas in a stainless steel autoclave at 170 to 190°C., using potassium hydroxide as a catalyst. At regular intervals samples of polyethenoxy tallate were removed, and soil removal and whiteness retention were determined. The effect of polyethenoxy chain length upon soil removal is illustrated in Figure 1 and upon whiteness retention in Figure 2. From these data it would appear that the polyethenoxy chain length has a pronounced effect upon detergency, that the minimum chain length for optimum soil removal is approximately 13 to 14 ethenoxy units, and that for optimum whiteness retention 14 to 15 ethenoxy units are desirable.

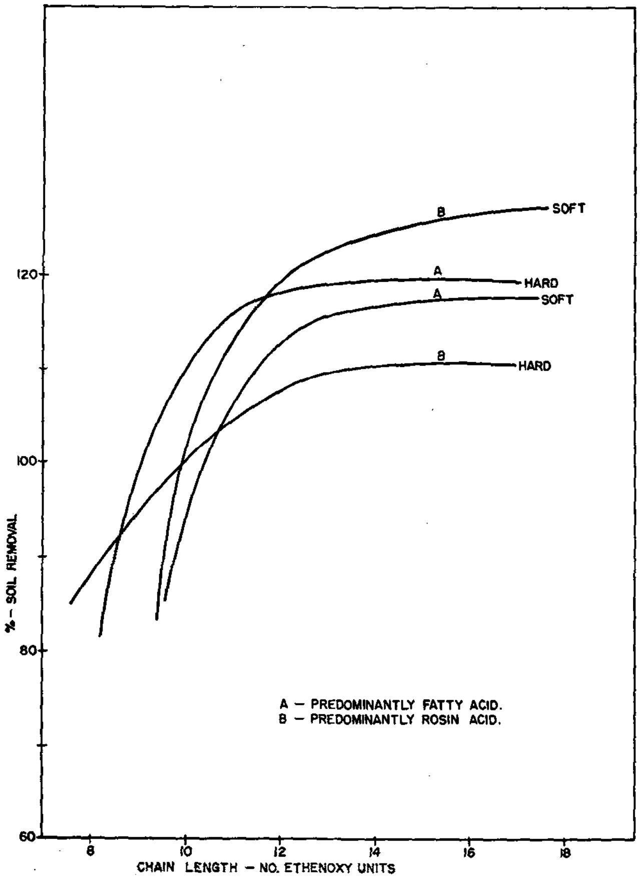

FIG. 1. Variation in soil removal in hard and soft water with ethenoxy chain length.

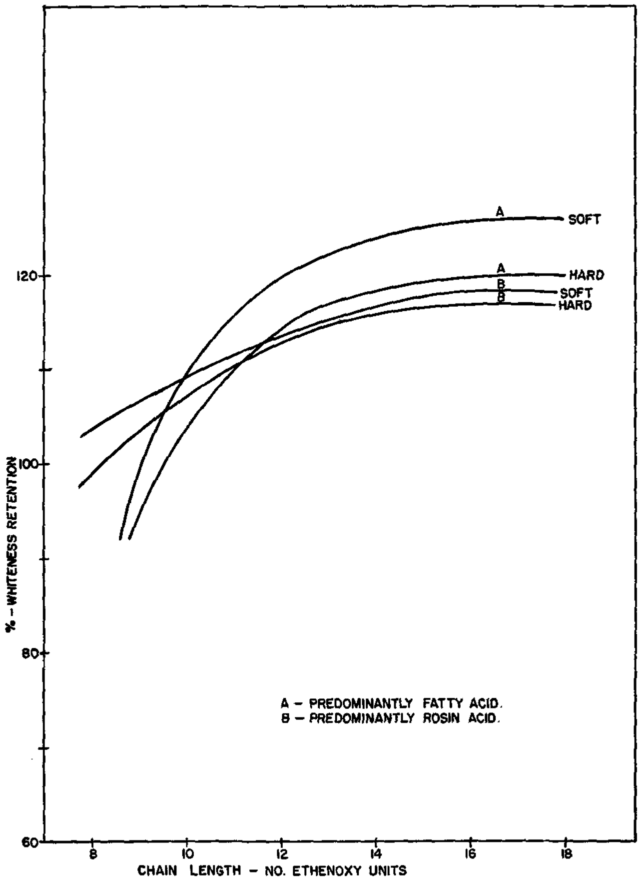

FIG. 2. Variation in whiteness retention in hard and soft water with ethenoxy chain length.

### Determination of Molecular Weight and Number of Ethenoxy Groups on Polyethenoxy Tallates

The degree of substitution of the tall oil with ethylene oxide was usually determined by accurately weighing the ingredients and the final product. However it seemed desirable to determine the average molecular weight independently. Hence a modification of the saponification equivalent method (6) was used. For this purpose approximately 5 g. of polyethenoxy tallate was weighed accurately into a round-bottom, standard-tapered flask, and a weighed excess (ca. 50%) of $N$ potassium hydroxide solution in diethylene glycol was added and the mixture allowed to reflux for two hours. The excess potassium hydroxide was back-titrated with standard N/4 hydrochloric acid, using a Beckman pH meter and magnetic stirring. In each case a pH titration curve was drawn and the end-point obtained graphically. The average molecular weight (saponification equivalent) was calculated using the conventional formula:

$$\text{Mol. Wt. (S.E.)} = \frac{(\text{Wt. Sample} - \text{Wt. Sample} \times \%\,\text{Sterol}/100)\,1{,}000}{\text{ml.} \times N\,\text{KOH} - \text{ml.} \times N\,\text{HCL}}$$

Since most tall oils contain from 5-10% of sterol or other inert materials, a correction factor was introduced into the above equation. The average number of ethylene oxide groups in a sample of tall oil was obtained by subtracting the average molecular weight of the original tall oil from that obtained from the saponification equivalent determined above and dividing the difference by 44, *i.e.*, the molecular weight of ethylene oxide. Table II lists molecular weights on a number of polyethenoxy tallates prepared in this laboratory and varying in their tall oil composition from predominantly fatty acids to those containing mostly rosin acids. The molecular weights determined by the above saponification method are compared to molecular weights obtained from actual weights of tall oil and ethylene oxide used.

TABLE II
Molecular Weights of Various Samples of Polyethenoxy Tallates

| Sample No. | From actual weights of tall oil and ethylene oxide | Determined by the saponification equivalent |
|---|---|---|
| 1 | 864 | 830 |
| 2 | 864 | 865 |
| 3 | 879 | 887 |
| 4 | 867 | 890 |
| 5 | 1,200 | 1,250 |
| 6 | 900 | 972 |
| 7 | 873 | 825 |
| 8 | 873 | 898 |
| 9 | 906 | 905 |

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# Application of Tracer Techniques to Studies on Autoxidation Reactions[1]

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THE autoxidation reactions of the fatty acids and esters involve intricate mechanisms, possibly of varied types. The voluminous literature (1) without much clarification of the picture for more than a century will add confirmation to the point. The actual advancement of our knowledge in this field may be attributed to the research carried on since 1936 by virtue of the advantages available to the present-day chemist, especially the tools from the school of physics and physical chemistry. Furthermore the approach to the studies on the mechanisms of autoxidation through reactions of oxygen with the simpler and known compounds, methyl oleate, linoleate, and linolenate, has facilitated such progress. Following these modern trends, it is felt that tagging of these simpler compounds with the suitable tracer isotopes may help to reveal some aspects of the mechanisms of autoxidation. However in the initial studies (2) autoxidation of methyl 9,10-dideutero-oleate gave results apparently contradictory to the general expectation, and no definite conclusions were reached. Contrary to expectations, dideutero-oleate showed a much longer induction period than oleate. It was not known whether the induction periods were due to trace impurities or were inherent properties of the compounds. The purification of these compounds through chromatography did not change such induction periods. Moreover deuterium contents of the water, volatiles, and residues of dideutero-oleate were unexpectedly uniform, calculated on a percentage basis. The purpose of the present paper is to show that these apparent contradictions are the indirect guides to the goals originally sought and may be correlated to the existing information on autoxidation of mono-olefinic substances.

Tracer techniques have been used in different chemical and biological reactions with good results but have not been used in autoxidation reactions before. The isotopes that can be used in the studies of autoxidation reactions of fatty acids and their esters are: deuterium, ($^{2}_{1}H \sim D$); heavy oxygen, $^{18}_{8}O$; stable carbon isotope, $^{13}_{6}C$; radioactive carbon isotope, $^{14}_{6}C$. Deuterium (99.0-99.5% pure) may be used for such studies. Heavy oxygen, to present knowledge, cannot be obtained in a purer state than 70 to 80% concentration and is used only in special cases involving decomposition of peroxides. When heavy oxygen in pure form becomes available, its use may throw some light on the intricate chemistry of the peroxides. The stable isotope $C^{13}$ and the radioactive isotope $C^{14}$ can play important roles in autoxidation studies, especially in locating the point of scission of the carbon chain during such reactions.

From the free radical mechanism of autoxidation reactions, the positions most involved are the carbon and H atoms of the double bond and of the methylene group alpha to the double bond. The methylenic group alpha to the carboxyl group, though very reactive in organic ionic reactions, has been neglected in autoxidation reactions. Tracer techniques may possibly detect these positions of reactivity. Two different alpha methylene C-atoms in the same molecule may be differentiated by incorporating radioactive $C^{14}$ in one position and stable $C^{13}$ in the other.

The methylenic group alpha to double bonds in methyl oleate or octadecene tagged with deuterium (3) $C^{14}$ or $C^{13}$ may be obtained from the 8-C ester via alcohol, bromides, etc. The other positional isomers may be synthesized by choice of proper fragments. Such synthesis has already been accomplished (4-7). The recent synthesis of linoleic acid by work-

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