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Tall Oil Studies. II. Decolorization of Polyethenoxy Tallates with Ozone and Hydrogen Peroxide

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DURING a study on the production of nonionic detergents in this laboratory by the condensation of ethylene oxide with various grades and samples of tall oil (1), a product of the paper pulp industry, the resultant products were contaminated with a dark brown coloration sometimes exhibiting a greenish fluorescence. Decolorization of these products however could not be effected by the usual means, such as the use of various chemical decolorizing agents or adsorption with activated charcoals or other adsorbents. It was also evident that tall oils of various compositions and origins gave products which varied in the intensity of this contaminant coloration: in general, those tall oils containing a larger proportion of rosin acid developed substantially darker colors and were more difficult to decolorize than those containing a larger proportion of fatty acids. This led us to suspect that the color formation might be caused by oxidation of the rosin acid perhydrophenanthrene ring to unsaturated quinoid phenanthrene derivatives which would be capable of resonance and hence color formation. Since the resonating structures might be decolorized by peroxidation with a reagent such as hydrogen peroxide or by ozonization, both reagents were tried and found successful in removing the color from the polyethenoxy tallates. The details of the decolorization of the tall oil-ethylene oxide nonionic detergents are described herein.

Experimental

Preparation of Polyethenoxy Tallates. A three-necked flask with standard-tapered ground glass joints was fitted with a fritted-glass gas inlet tube, a thermometer, and an outlet tube. The flask was externally heated with a glas-col mantle, and provisions were made for convenient weighing of the flask and its contents during the actual condensation. Various compositions and grades of tall oil (100 g.) (see Table I) were placed in the flask with 0.5 g. of potassium carbonate catalyst and heated to 190°C. with a current of nitrogen gas flowing through the mixture. At 190° the passage of nitrogen was discontinued, and ethylene oxide gas was bubbled through the liquid. The excess was vented through the outlet tube. The temperature generally increased with the heat of the reaction and was maintained between 170-210°C. When a total weight of 200 g. of ethylene oxide had been taken up by the tall oil, the gasification was discontinued, the polyethenoxy tallate was allowed to cool to room temperature, and the dark-colored fluorescent product was decolorized with hydrogen peroxide and ozone as described below:

TABLE I

Preparation of Polyethenoxy Tallates

Exp. No.	Composition Ratio		Approx. Molecular Weight		% Transmission (Red Filter)
	Rosin Acid	Fatty Acid	Tall Oil	Polyethenoxy Tallate	
A	10	90	289	867	48
B	30	70	288	864	47
C	45	55	291	873	38
D	55	45	293	879	24
E	90	10	300	900	4

Twenty grams of each sample of polyethenoxy tallate (Table I) were weighed into a Coleman colorimeter test tube, and the intensity of the color was measured on a Coleman electric colorimeter, Model 8, with a red filter No. 8-215, using the null method with the reading for distilled water arbitrarily set at 100% transmission. A transmission value of 90% was considered desirable for adequate decolorization of the products.

Ozone Generator. Ozone was generated in the usual manner by passing oxygen through an air space charged with an alternating current potential of 15,000 volts, using as an inner electrode a mercury column and copper sulfate solution as the outer electrode. The amount of ozone generated varied with the rate of flow of oxygen so that the ozonizer had to be calibrated at room temperature, using potassium iodide solution to trap the ozone for a 30-second period. The iodine formed was back-titrated with 0.01 *N* sodium thiosulfate solution, using starch indicator. A calibration curve for the ozonizer was constructed in which the rate of flow of oxygen *vs.* % ozone generated was constructed. The volume of ozone was calculated from this curve in all the succeeding experiments.

Ozonization of Polyethenoxy Tallates. Ozone was passed into each of the five tallate samples (Table I) in colorimeter tubes at a measurable rate, and the decolorization was measured quantitatively in the Coleman instrument as described above. The values for % transmission *vs.* ml. ozone required for 20-g. tallate samples are depicted in Figure 1, and the actual volume of ozone required to decolorize the tallates to a 90% transmission value at room temperature is recorded in Table II. It seems that the amount of ozone necessary for decolorization increases directly with the rosin acid content.

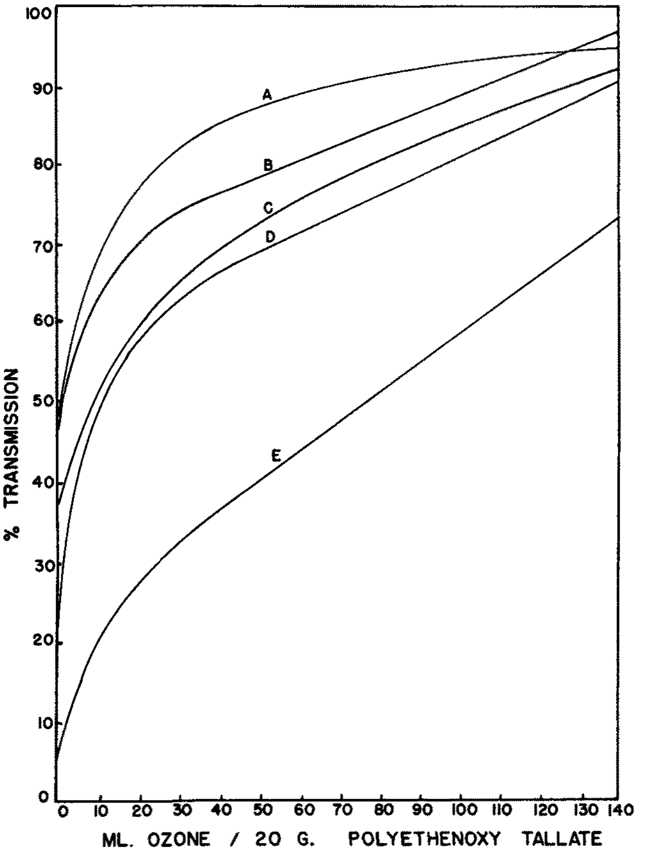


FIG. 1. Decolorization of polyethenoxy tallates with ozone (See Table I).

TABLE II

Polyethenoxy Tallate Sample No.	ml. Ozone Required to Decolorize 20 g. Sample to 90% Transmission	ml. Ozone Required to Decolorize 20 g. Peroxide-Treated Sample to 90% Transmission
A	65	20
B	107	55
C	130	95
D	140	160*
E	170*	220*

* Extrapolated Values.

Treatment of Polyethenoxy Tallates with Hydrogen Peroxide. Into each of the five tallate samples (20 g.) 30% hydrogen peroxide was added with micropipets in increasing quantities. After each addition of peroxide the mixture in the colorimeter tube was stirred for five minutes at room temperature and read in the Coleman instrument. The extent of decolorization as determined from % transmission was plotted against the ml. of 30% hydrogen peroxide in Figure 2. From Figure 2 it becomes quite evident that those tallate samples with the least amount of rosin acid (A and B) are decolorized to a lighter color than those with an intermediate quantity of rosin acid (C and D), and the sample with the largest proportion of rosin acid (E) was most difficult to decolorize.

Further Decolorization of Peroxide-Treated Polyethenoxy Tallates with Ozone. Progressive quantities of ozone at room temperature were passed into 20-g. tallate samples, previously decolorized with 0.2 ml. of 30% hydrogen peroxide, and transmission values were measured. The decolorization of peroxide-treated tallate samples is shown in Figure 3, and the amounts of ozone required for each sample to a 90% transmission value are recorded in Table 2. Figure 3 further illustrates the fact that tallates with larger percentages of rosin acid are more difficult to decolorize. It is also evident that approximately 55 ml. of ozone or less was required for peroxide-treated samples of tallates richer in fatty acids (A and B).

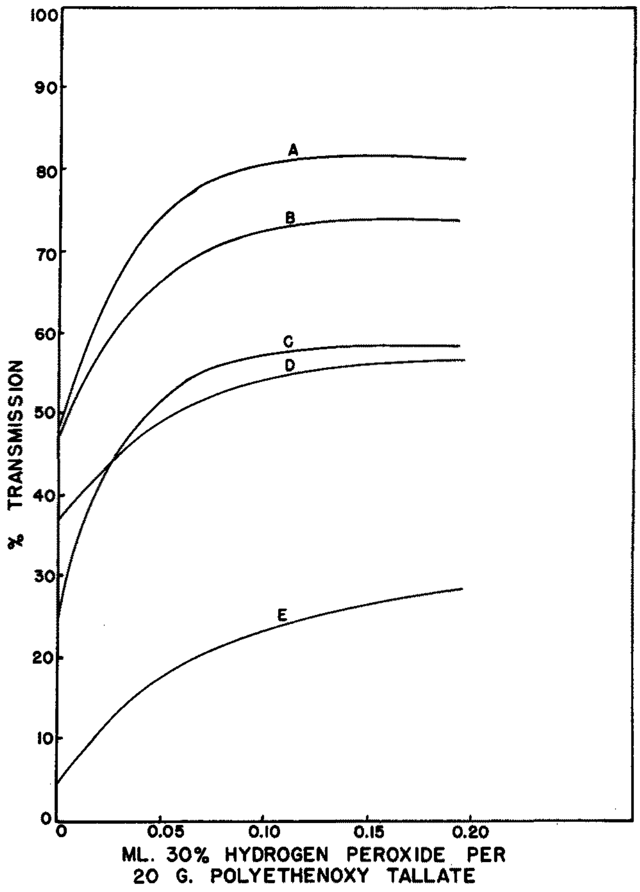


FIG. 2. Decolorization of polyethenoxy tallates with 30% hydrogen peroxide (See Table I).

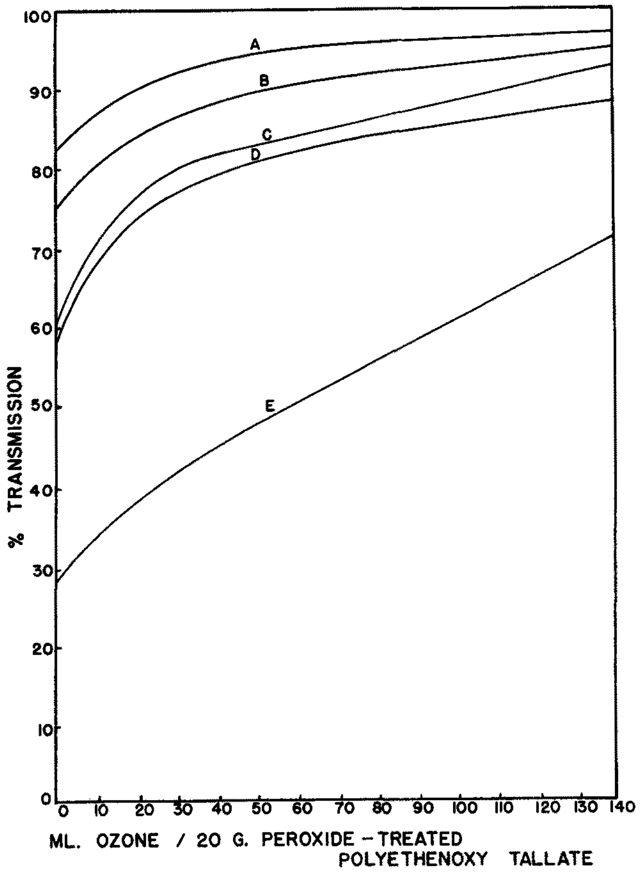
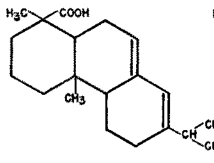


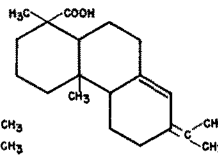
FIG. 3. Decolorization of peroxide-treated polyethenoxy tallates with ozone (See Table I).

Discussion of the Chemistry Involved in the Decolorization of Polyethenoxy Tallates by Ozone and Hydrogen Peroxide

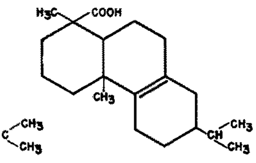
Polyethenoxy tallates, *i.e.,* ethylene oxide condensation products of tall oil consist of a mixture of polyglycol esters of rosin and fatty acids. The rosin acids consist of a mixture (2) of at least seven acids isomeric with abietic acid (I); the proportions of each acid varies with the origin and processing of the tall oil. The various isomeric rosin acids differ from abietic acid in the number and position of the double bonds. Thus along with abietic acid (I), which represents approximately 40% of the rosin acid fraction, neoabietic acid (II) and dihydroabietic acid (III) are also reportedly present to the extent of 20% and 14%, respectively.



I



II



III

The fatty acid fraction also consists of a mixture of approximately equal amounts of oleic (IV) and linoleic acids (V) along with a trace of palmitic acid (VI).

$$CH_3{-}(CH_2)_7{-}CH{=}CH{-}(CH_2)_7{-}COOH$$

IV

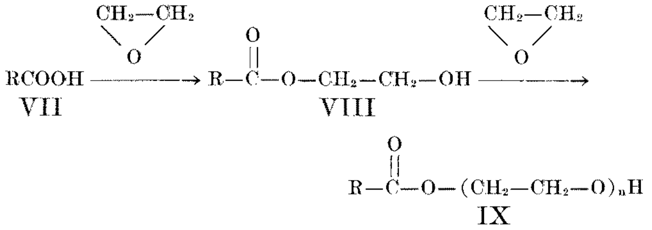
$$CH_3{-}(CH_2)_4{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2)_7{-}COOH$$

V

$$CH_3{-}(CH_2)_{14}{-}COOH$$

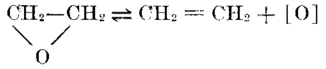
VI

The 10 or more acids present in tall oil therefore have the carboxy group in common and can be represented by the general formula RCOOH (VII). The esters of this mixture of acids are simply designated as tallates. These acids can be esterified first with one mole of ethylene oxide in the presence of alkaline catalysts, and the intermediate polyethenoxy tallates (VIII) so produced, though not isolated, are etherified with progressive quantities of ethylene oxide, according to the previously suggested mechanism (3), until the polyethenoxy tallates (IX) become water soluble.



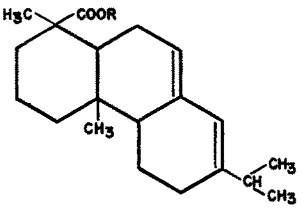
$$\underset{VII}{RCOOH} \xrightarrow{\underset{O}{CH_2{-}CH_2}} \underset{VIII}{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}OH} \xrightarrow{\underset{O}{CH_2{-}CH_2}} \underset{IX}{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}(CH_2{-}CH_2{-}O)_nH}$$

In most of the esters prepared herein (Table I) n is approximately 12 to 14 ethenoxy units. What apparently happens however is that not all of the ethylene oxide is used up in the esterification and etherification, but under the experimental conditions described above some of the ethylene oxide may revert back to ethylene and oxygen, and this oxygen would tend to dehydrogenate

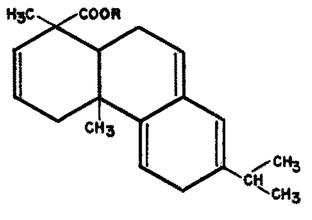


$$\underset{O}{CH_2{-}CH_2} \rightleftharpoons CH_2 = CH_2 + [O]$$

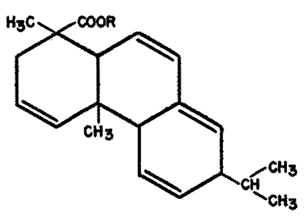
or oxidize the rosin esters to unsaturated phenanthrene structures with resonating quinoid forms. To substantiate further the supposition that rosin acids are responsible for the color formation, pure abietic acid was condensed with ethylene oxide whereupon an extremely dark product was obtained. Using the oxidation of polyethenoxy abietiate (X) as an example, at least three unsaturated forms capable of resonance (XI, XII, and XIII) may be written which would certainly be highly colored.



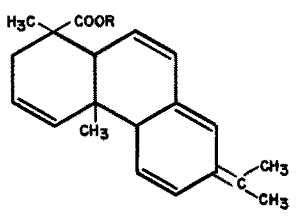
X



XI



XII

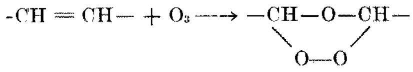


XIII

R = POLYETHENOXY

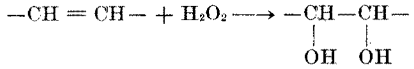
Any number of intermediate colored, quinoid forms could be written for the other rosin acids. All of these, incidentally, should be highly fluorescent.

The action of ozone on a double bond in general may be represented in the following manner:



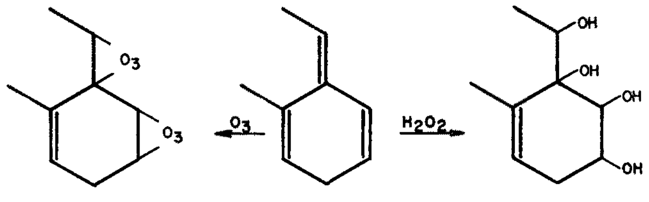
$$-CH=CH- + O_3 \longrightarrow \underset{\diagdown O-O \diagup}{-CH-O-CH-}$$

Hydrogen peroxide likewise adds to a double bond with ultimate formation of glycols after hydrolysis of intermediate oxide compounds (4).



$$-CH=CH- + H_2O_2 \longrightarrow -\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-$$

The double bond is replaced by an ozonide in the former case and by a glycol in the latter case. Thus a quinoid colored structure as represented by formula (XIV) should give a colorless ozonide (XV) or glycol (XVI).



XV XIV XVI

This in essence is a possible explanation for the discolorization of oxidized polyethenoxy tallates with ozone or hydrogen peroxide. From Figure 2 it appears that hydrogen peroxide is limited in the number of quinoid double bonds which it can sever while ozone is more effective. Actually, only a trace of quinoid structures need be prseent to give highly colored tallates, and the ozone or peroxide would add to the double bonds of the normal esters (IX, X) as well as to the quinoid structures. It should be noted that a decolorized product actually contains more oxygen and probably possesses greater water solubility than the parent tallate.

Summary

A method for decolorizing tall oil-ethylene oxide condensates (polyethenoxy tallates) by use of ozone or hydrogen peroxide is presented. The chemistry of the possible reactions involving quinoid structures is discussed.

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Report of Glycerine Analysis Committee–September 1953

THE collaborative program for analysis of glycerine, which included 33 laboratories in this country and abroad, was continued this year in conjunction with the Special Committee on Glycerine. The average result for the analyses of the collaborative samples and the precision of the analyses as expressed by the standard deviation are given in the following table.

In view of the interest in the sodium periodate method in this country and abroad as a replacement for the acetin method, we plan to conduct during the coming year some collaborative tests by the official A.O.C.S. Method Ea 6-51 and modifications that have been suggested by collaborators abroad. The details for the 1954 program will be decided on at the fall meeting of the Glycerine Analysis Committee.

Some modifications of the total residue method directed toward simplifying and shortening procedure are being studied. The tests made this year look promising and will be continued.

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H. C. BENNETT W. A. PETERSON
E. L. BOLEY J. B. SEGUR
W. C. CLARK ARNOLD TROY
W. D. POHLE, chairman

Summary of Averages and Standard Deviations for Collaborative Results for 1952-1953

	Average	Standard dev.	2 Sigma units
C. P. Glycerine			
Glycerol Ea 4-38 (Acetin)	94.39	0.43	93.53 -95.25
Ea 6-51 (Na Period.)	95.10	0.30	94.50 -95.70
Ea 7-50 (Sp. Gr.)	95.04	0.13	94.78 -95.30
Soap Lye Crude No. 2			
Ash	9.18	0.31	8.56 - 9.80
Total alkalinity	0.85	0.07	0.71 - 0.99
Free alkalinity	0.030	0.014	0.002- 0.058
Combined alkalinity	0.75	0.05	0.65 - 0.85
Carbonate	0.09	0.04	0.01 - 0.17
Salt	7.14	0.08	6.98 - 7.30
Total residue	10.71	0.61	9.49 -11.93
Organic residue	1.66	0.57	0.52 - 2.80
Glycerol Ea 4-38	80.41	0.58	79.25 -81.57
Ea 6-51	80.49	0.43	79.63 -81.35
Saponification Crude No. 3			
Ash	3.89	0.20	3.49 - 4.29
Free acidity	0.06	0.014	0.03 - 0.09
Total alkalinity	0.24	0.09	0.06 - 0.42
Alkalinity equiv	0.42	0.15	0.12 - 0.72
Salt	0.12	0.13	- 0.38
Total residue	15.46	0.83	13.80 -17.12
Organic residue	11.68	1.10	9.48 -13.88
Glycerol Ea 4-38	79.62	1.32	76.98 -82.26
Ea 6-51	80.28	0.37	79.54 -81.02