Illinois Academy of Science Transactions, Vol. 47, 1955

COMPARATIVE ANALYSES OF POLYETHENOXY TALLATES

A. T. BALLUN, G. E. BARTELS, AND J. V. KARABINOS
Blockson Chemical Company, Joliet

In a previous article[1] the preparation of polyethenoxy tallates, condensation products of tall oil with ethylene oxide, was described along with their comparative detergency in built mixtures. In that study, the extent to which the ethylene oxide condensed with various tall oil samples was determined by use of the saponification equivalent. Subsequently, it became desirable to study other analytical procedures for the analyses of these nonionic esters and, if possible, to select a more suitable method. The methods consisted of (A) the saponification equivalent, (B) carbon and hydrogen analyses and (C) the iodine number; they were carried out on polyethenoxy tallates of different molecular proportions.

Preparation of Polyethenoxy Tallates

For these experiments, a commercial tall oil (triple-distilled Indusoil, West Virginia Paper & Pulp Co.) was selected which contained approximately 69% fatty acids, 29% rosin acids and 2% unsaponifiables. The tall oil was admixed with 0.5% of its weight of anhydrous 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 a rate that maintained the temperature between 160-190°C. The amount of gas absorbed was determined periodically by weighing the flask and its contents, and polyethenoxy esters containing from 6 to 22 moles of ethylene oxide per mole of tall oil were synthesized (table 3). The various analytical procedures described below were carried out on these samples.

Method A. The Saponification Equivalent

The most likely method for the analysis of these esters would seem to be the determination of their saponification equivalent. The chief difficulty lies in the quantitative saponification of the rosin esters, which account for approximately 29% of the tall oil content. For this reason, the saponification was carried out at higher temperatures using one normal potassium hydroxide in diethylene glycol solution. A 5-gram sample of nonionic ester was refluxed for 4 hours with an excess of the alkali, diluted with an equal volume of ethanol, and, on cooling, the excess alkali was back-titrated with 0.25 *N* hydrochloric acid, using a pH meter to determine the change in acidity. A pH titration curve was constructed whereby the excess of alkali was ascertained by graphical interpretation of the curve. The end

[1] E. M. Stoltz, A. T. Ballun, H. J. Ferlin, and J. V. Karabinos, Jour. Am. Oil Chem. Soc., 30, 271 (1953).

point was generally obtained at pH 9.2 to 9.4. The number of ethylene oxide units (n) of the nonionic ester was calculated as follows:

$$n = \frac{\text{(wt. sample x 1000)} \quad 289}{44\ (\text{ml. x N KOH} - \text{ml. x N HCl}) \quad 44}$$

The number of ethylene oxide units in each polyethenoxy tallate was determined by this method; the results are compared in table 3 with the other methods.

Method B. Carbon and Hydrogen Analyses

It seemed logical that since the oxygen content of the tall oil was approximately 11% and that of ethylene oxide was 36%, the introduction of additional ethenoxy units would lower the carbon and hydrogen content of the nonionic esters. Hence, carbon and hydrogen analyses of the products should provide a measure of the ethylene oxide content. However, the carbon and hydrogen content of the original tall oil must be known with some certainty. The various constitutents in the tall oil used in these condensations had been reported,[2] and from these a tentative formula was calculated (table 1). A carbon and hydrogen analysis was performed on this tall oil and exceptionally good agreement was obtained.

Thus, from the above analytical data an empirical formula of $C_{18.66}H_{32.67}O_{1.98}$ was obtained for triple-distilled Indusoil. From these figures, theoretical percentages of carbon (77.61%) and hydrogen (11.41%) were calculated. By combustion analysis, carbon values averaged 77.55% and hydrogen values of 11.09% were obtained on this

[2] F. J. Ball and W. G. Vardell, Jour. Am. Oil Chem. Soc., 28, 137 (1951).

Table 1.—Calculation of Carbon and Hydrogen Content of Tall Oil[a]

Constituent	Mole fraction	Empirical formula	Proportions of		
			Carbon	Hydrogen	Oxygen
Oleic acid	0.310	$C_{18}H_{34}O_2$	5.58	10.54	
Linoleic acid	0.331	$C_{18}H_{32}O_2$	5.96	10.59	
Palmitic acid	0.048	$C_{16}H_{32}O_2$	0.77	1.53	
Abietic acid, Neoabietic acid, Levopimaric acid	0.148	$C_{20}H_{30}O_2$	2.96	4.44	
Dihydroabietic acid, Dextropimaric acid	0.087	$C_{20}H_{32}O_2$	1.74	2.78	
Tetrahydroabietic acid	0.041	$C_{20}H_{34}O_2$	0.82	1.39	
Dihydroabietic acid	0.015	$C_{20}H_{28}O_2$	0.30	0.42	1.96
β-Sitosterol	0.010	$C_{29}H_{48}O$	0.29	0.48	0.01
Lignoceryl alcohol	0.010	$C_{24}H_{50}O$	0.24	0.50	0.01
			18.66	32.67	1.98

a) Triple distilled Indusoil.

starting material; these figures were used as a basis for further calculation of the ethenoxy content. For example, an empirical formula for the ester containing six ethylene oxide units was determined by adding $C_{12}H_{24}O_6$ (*i.e.* 6 x C_2H_4O) to the above formula for tall oil. The percentage carbon in the resultant ester was calculated. In this way, the carbon content of tall oil esters containing from 6 to 23 ethylene oxide units were calculated and a graph was constructed in which the carbon content vs. ethenoxy units were plotted. From this curve (fig. 1) knowing the percent carbon of the ester by the combustion method, one can read off the ethylene oxide content of the nonionic ester. Table 2 indicates the actual percentages of carbon and hydrogen obtained experimentally on the various tall oil-ethylene oxide condensates in comparison with calculated C and H values.

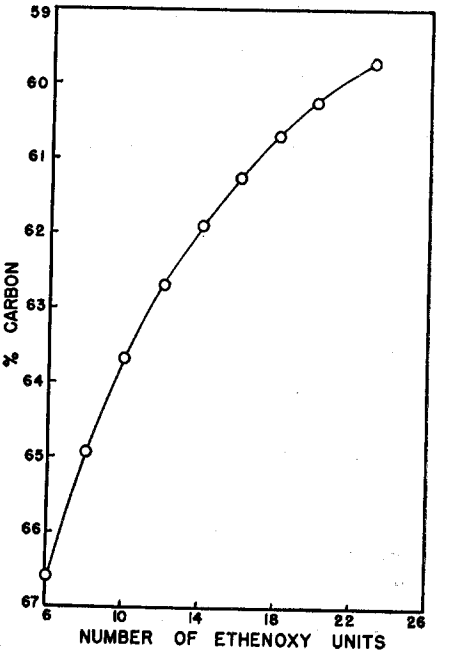

FIG. 1.—Variation in carbon content with ethenoxy chain length of a tall oil nonionic.

From the values in table 2, it becomes evident that only the carbon content is of any value in ascertaining ethenoxy content since the experimental error in determining carbon and hydrogen is usually considered to be in the neighborhood of ± 0.2%.

The ethenoxy content of the synthetic esters determined from the carbon analyses with the aid of fig-

TABLE 2.—CARBON AND HYDROGEN ANALYSES OF NONIONIC ESTERS.

Number of Ethenoxy units	Calculated values		Ester	Actual values	
	% C	% H		% C	% H
6	66.58	10.33	A	66.09	9.96
8	64.92	10.17	B	64.31	10.01
10	63.67	10.04	..	.....	.....
12	62.68	9.95	C	62.67	10.04
14	61.90	9.87	D	61.94	9.55
16	61.24	9.81	E	61.17	9.59
18	60.69	9.75	F	60.75	9.90
20	60.26	9.69	G	60.08	9.35
23	59.68	9.66	H	59.90	9.64

TABLE 3.—COMPARATIVE ANALYSES OF POLYETHENOXY TALLATES.

Nonionic detergent	Number of Ethenoxy Units				
	From Weight of materials	From Saponification equivalent	From carbon analyses	From iodine number	Average
A	6	6.5	6.6	6.8	6.5
B	8	8.1	8.9	9.50	8.6
C	12	12.0	12.0	12.0	12.0
D	13.2	13.1	13.9	13.5	13.4
E	15.2	13.9	16.2	16.6	15.5
F	17.1	15.0	17.7	18.5	17.1
G	19.1	18.6	20.6	23.1*	19.4
H	22.9	21.9	21.6	23.8	22.5

* Discarded.

ure 1 is listed in table 3 in comparison with that obtained by other analytical procedures.

METHOD C. IODINE TITRATION

Since tall oils generally contain unsaturated linkages, and this particular one possessed an iodine number of 181, addition of ethylene oxide reduces the iodine number of the product proportionally. The analysis for iodine number was carried out by the AOAC[3] procedure.

In a typical analysis, a 0.2 g. sample is weighed into a glass stoppered flask and 25 ml. of iodine monochloride solution (Wijs) is added, and the mixture is allowed to stand for one hour in a dark place with occasional shaking. Ten ml. of potassium iodide solution and 100 ml. of water are added and the mixture is titrated with standard sodium thiosulfate solution. The iodine number is reported as the number of centigrams of I required for one gram of fat. From the iodine number of the original tall oil ($I_{T.O.}$ in this case 181), the molecular weight of the tall oil ($M.W._{T.O.}$ in this case 289) and the iodine number of the ethenoxy ester (I_E), the number of ethylene oxide units (n) in the ester may be calculated as follows:

$$n = \frac{I_{T.O.} \frac{x}{I_E} M - M_{T.O.}}{44}$$

The actual values for the number of ethylene oxide units as determined by the iodine method are listed in table 3.

The average values obtained herein were employed in the succeeding work on physical properties of these nonionic esters.[4]

CONCLUSIONS

Nonionic detergent esters were synthesized and examined in several different ways for their ethenoxy content. It became evident that as the molecular weight increased, the

[3] "Methods of Analysis of the Association of Official Agricultural Chemists," ed. 5, AOAC, Washington, D. C., 1940, p. 95.

[4] V. Cronin et al., Trans. Ill. Acad. Sci., vol. 47 (1955).

precision of each analysis decreased. From the standpoint of time and accuracy, it is recommended that the iodine-number method be used for the determination of ethenoxy content of these esters, particularly with esters of lower molecular weight. With those of higher molecular weight, it seems desirable to use the weights of the starting materials and final product to determine the degree of substitution.