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CORRELATION OF DETERGENCY OF POLYETHENOXY TALLATES WITH PHYSICAL PROPERTIES

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Soaps and detergents usually possess hydrophilic and hydrophobic radicals in the same molecule, which reduces surface tension and aids in the emulsification and removal of soil. Soap itself consists of such groups—the fatty acid chain represents the hydrophobic portion and the sodium salt the hydrophilic unit. In order to combat hard water (reduce the precipitation of insoluble calcium and magnesium salts), organic sodium sulfonates or sulfates have been used as hydrophilic groups. A more recent innovation, however, particularly for automatic washing machines to improve sudsing qualities, has been the replacement of hydrophilic ionic-type groups by a water-loving long chain, polymerized ethylene oxide, which is nonionic and is referred to as a polyethenoxy or polyoxyethylene radical.

The synthesis of such nonionic detergent esters from tall oil fatty acids, inexpensive by-products of the Kraft paper pulp industry, and ethylene oxide was reported in an article on p. 81[1], along with various analytical procedures for determining their ethenoxy content. This article is concerned with the determination of various physical constants of these esters in comparison with detergency tests for purposes of correlation. Physical properties studied included refractive index, specific gravity, viscosity, surface tension, and freezing point measurements on tall oil esters containing from 6 to 23 moles of ethylene oxide.

Analytical Procedures

Refractive index measurements were carried out with a Bausch and Lomb Abbe refractometer; and a temperature of 35° C was maintained by circulation of 35° C water from a constant temperature bath.

Specific gravity determinations were made at 35° C using 10 and 25 ml. pycnometers which had previously been calibrated with distilled water.

Viscosity measurements were made with a Stormer viscosimeter standardized with water-glycerol mixtures. The measurements were carried out at 35° C by use of the constant temperature bath.

Surface tension values were obtained using a du Nuoy tensiometer on 1% and 0.1% aqueous solutions of each nonionic ester.

Freezing point. Time-temperature cooling curves were carried out

[1] A. T. Ballun, G. E. Bartels, and J. V. Karabinos, Trans. Ill. Acad. Sci., vol. 47 (1955).

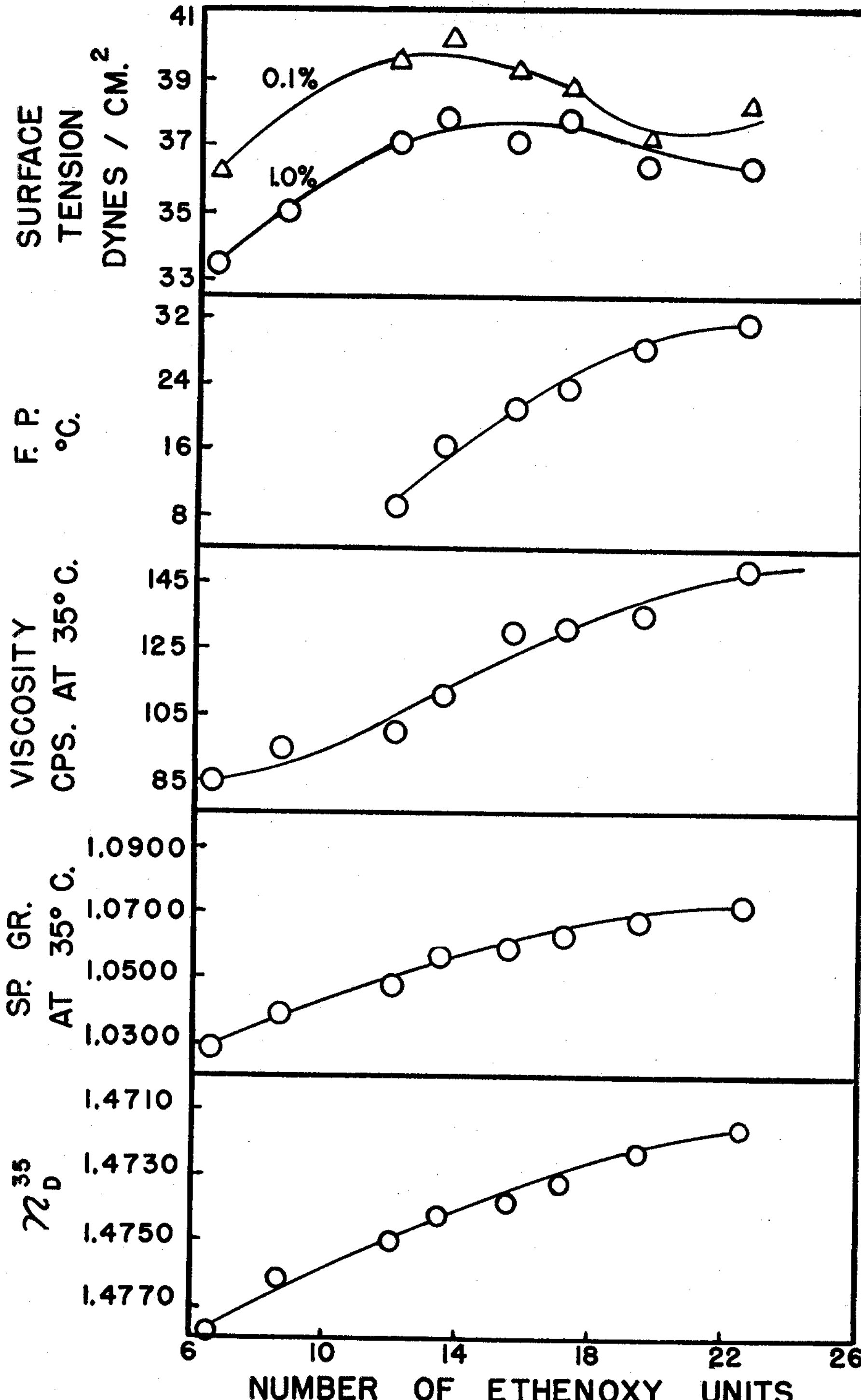

FIG. 1.—Correlation of physical properties with ethenoxy chain length of a tall oil nonionic.

TABLE 1.—PHYSICAL PROPERTIES OF VARIOUS POLYETHENOXY TALLATES

Nonionic detergent	Number of ethenoxy units[a]	Refractive index N_D^{35}	Specific gravity @ 35°	Viscosity CPS @ 35°	Surface tension[b] dynes/sq. cm.	Freezing point °C
A	6.5	1.4779	1.0286	85	33.43	....
B	8.6	1.4762	1.0387	95	35.13	....
C	12.0	1.4750	1.0479	100	37.04	9.6
D	13.4	1.4742	1.0561	112	37.93	16.7
E	15.5	1.4738	1.0590	130	37.01	21.0
F	17.1	1.4732	1.0622	132	37.65	23.8
G	19.4	1.4723	1.0669	135	36.38	28.4
H	22.5	1.4717	1.0717	150	36.35	31.0

a) Average Values from Reference 1.
b) Surface tension in 1% aqueous solution.

on each ester; the freezing point was determined from the flat portion of the curve.

These physical measurements are recorded in table 1 and shown in fig. 1.

Detergency tests were carried out on the polyethenoxy tallates[2] by the previously described method[3]. Whiteness retention and soil removal were measured on cotton swatches by a Launderometer. The detergency tests were carried out on test mixtures containing 20% by weight of the polyethenoxy tallate, 20% tetrasodium pyrophosphate, 20% sodium tripolyphosphate, 39% soda ash, and 1% carboxymethylcellulose. All determinations were arbitrarily compared to a single standard set at 100%. For this purpose a commercially available structurally similar nonionic detergent mixture was chosen, and detergency of the test solutions and standard contained 0.25 g. of test mixture per 100 ml. of ester. The detergency tests on the synthesized nonionic esters are shown in figure 2.

DISCUSSION

The object of this study was to correlate detergency of polyethenoxy tallates of varying ethenoxy chain length with their physical properties. One may conclude from figure 1 that properties such as freezing point, viscosity, and specific gravity increase more-or-less proportionally with increasing molecular weight while the refractive index decreases. However, the surface tension curves follow a different course, increasing with increasing number of ethenoxy units until the optimum detergency has been reached at 12 to 14 ethylene oxide units. With further increase in molecular weight beyond this point the surface tension again seems to decrease. Thus, a peak is obtained in the surface tension curve at about the same point at which optimum detergency is reached. It is well known that surface tension plays some part in

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

[3] T. A. Vaughn and H. R. Suter, *Ibid.*, 27, 249 (1950).

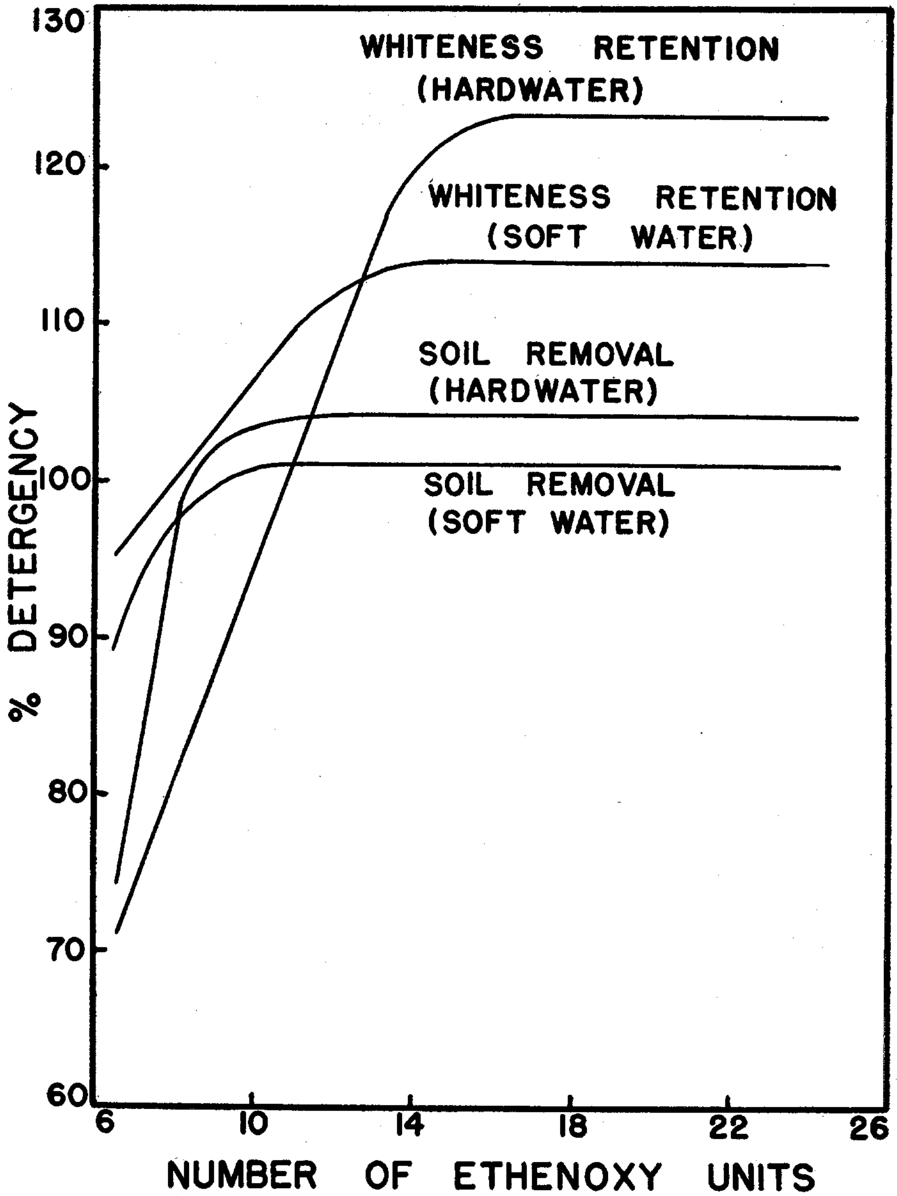

FIG. 2.—Correlation of detergency with ethenoxy chain length of a tall oil nonionic.

detergency and that, in general, reduction of surface tension of a washing solution with a surfactant aids in the removal of soil. It seems likely, therefore, that the surface tension curves herein obtained, as related to detergency, may have real significance.

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