New Nonionic Detergents Derived from Epoxidized Oils. III[1]

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Abstract

A series of 21 nonionic detergents based on epoxidized sperm oil, epoxidized methyl oleate, and epoxidized butyl tallate are discussed. The materials were synthesized by alcoholysis of the oxirane oxygen in the presence of boron trifluoride. Benzene was used as a solvent to act as a coupling agent for the unreacted materials. Methoxy polyoxyethylene alcohols were used as the hydrophilic alcohols with which the epoxidized esters were reacted. Physical properties and performance characteristics of the various compounds synthesized are catalogued and the reaction itself is characterized.

It is shown that the properties of the materials can be varied by varying both the size of the polyoxyethylene moiety attached to the ester and the characteristics of the ester itself. These materials all appear to be low foaming wetting agents and emulsifying agents. It is felt that these materials offer a definite potential for the use of epoxidized natural fats and natural fat derivatives for the custom synthesis of tailor made surface active agents. Being based on naturally occurring straight chain materials they would also be biologically degradable.

Introduction

THE INCREASING VARIETY of commercially available epoxidized oils and esters has made available a large number of reactive hydrophobic molecules which can be fashioned into a variety of nonionic surface active agents. Although the laboratory methods used in this study would require extensive equipment investments if carried out on a commercial scale, it is felt that appropriate synthetic methods can be worked out whereby a prospective user of nonionic polyoxyethylene based detergents could synthesize them in simple equipment and match their characteristics to his individual needs. The materials presented here are representatives of but a few of the many materials that can be produced in this manner.

Materials

Samples representing commercial production of epoxidized butyl tallate, epoxidized methyl stearate and epoxidized sperm oil having oxirane oxygen contents of 5.34%, 4.70% and 3.84% were obtained (Table I). These figures represent equivalent weights of 300, 340, and 417, respectively. Boron trifluoride, dihydrate, Lot No. VO16 was obtained from the General Chemical Division of the Allied Chemical Corporation. The methoxy polyoxyethylene alcohols (Table II) were obtained from the Nitrogen Division of the Allied Chemical Corporation. They ranged in average hydroxyl equivalent weight as determined by ASTM Method D-1957-61T from a low value of 155 to a high value of 1046 in increments of approximately 150. Reagent grade (A.C.S.) benzene was used as the coupling solvent.

TABLE I

Characteristics of Epoxidized Esters

Starting ester	% Oxirane oxygen	Equivalent wt.	Iodine value	Index of refraction N_{D-}^{30}
Methyl oleate	4.70%	340	1.6	1.4522
Butyl tallate	5.34%	300	3.2	1.4491
Sperm oil	3.84%	417	2.2	1.4600

Experimental

Benzene equivalent to one half the combined weight of the two reacting moieties was added to the reaction vessel shown in Figure 1. The appropriate polyglycol and the boron trifluoride dihydrate were then added and the Squibb funnel containing the epoxidized ester was put in place. The system was heated to reflux temperature and the water from the boron trifluoride dihydrate and the methoxy polyoxyethylene alcohol was azeotropically removed. After removal of the water as indicated by cessation of water collection, the epoxidized ester was slowly added to the refluxing mixture. Reflux was continued for one hour after all the epoxidized ester had been added.

The product containing the benzene from this first step was placed in a flash evaporator at a pressure of 200 to 500 μ for 2 hr while the flask was immersed in an 80C water bath. A small amount of water (approximately one-fifth that of the original benzene present) was added to the flask during the last hour of the evaporation period to complete removal of the benzene.

Physical Characteristics

The characteristics of the products are shown in Table III. The solubility, refractive index and vis-

TABLE II

Polyethylene Glycol Methyl Ethers Physical Properties

Physical property	Polyethylene glycol methyl ether						
	150	300	450	600	750	900	1050
Average molecular weight	155	302	410	580	750	855	1046
Color APHA	10	5–10	5–10	0–5	0–5[a]	5[a]	5[a]
Viscosity, Sus at 210F	33.9	39.4	43.9	54.0	63.5	73.8	86.8
pH, 5 wt% aqueous sol.	5.5	6.9	6.5	6.8	6.8	6.6	6.9
Acidity, wt% as acetic acid	0.005	0.005	0.003	0.0087	0.0142	0.0205	0.0078
Basicity, wt% as NAOH	0.014	0.021	0.02	0.028	0.026	0.028	0.029
Ash, wt%	0.001	....	0.01	......	0.028	......	0.033
Apparent specific grav. 20/20C	1.0496	1.0846	1.0967	1.1008[b]	......	......	. ....

[a] 25 wt% Aqueous solution.
[b] 26/20C.

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[1] Presented at the AOCS Meeting, New Orleans, April 1964.

TABLE III
Physical Characteristics

Molecular weight of alcohol	HLB (calculated)	Hydroxyl value	Physical form	Water solubility	Refractive index N_D^{50C}
Epoxidized methyl oleate derivatives:					
155	6.3	76	Liquid	Insoluble	1.4471
302	9.4	71	Liquid	Insoluble	1.4479
410	10.9	56	Liquid	Partly solub.	1.4499
580	12.6	47	Liquid	Soluble	1.4511
750	13.8	47	Paste	Soluble	1.4519
855	14.3	44	Paste	Soluble	1.4532
1,046	15.1	35	Paste	Soluble	1.4542
Epoxidized butyl tallate derivatives:					
155	6.8	94	Liquid	Insoluble	1.4492
302	10.0	78	Liquid	Insoluble	1.4501
410	11.6	63	Liquid	Party solub.	1.4510
580	13.2	46	Liquid	Soluble	1.4531
750	14.3	48	Paste	Soluble	1.4538
855	14.8	41	Paste	Soluble	1.4547
1,046	15.5	37	Paste	Soluble	1.4556
Epoxidized sperm oil derivatives:					
155	5.4	83	Liquid	Insoluble	1.4542
302	8.4	68	Liquid	Insoluble	1.4536
410	9.9	59	Liquid	Partly solub.	1.4539
580	11.7	46	Liquid	Soluble	1.4545
750	12.9	42	Paste	Soluble	1.4554
855	13.4	44	Paste	Soluble	1.4556
1,046	14.3	37	Paste	Soluble	1.4564

cosity increase with increasing molecular weight and HLB while the hydroxyl value tends to decrease. HLB values were computed as suggested by Griffin (1).

Surface and Interfacial Tension Data

The surface tension and interfacial tension versus hexane and benzene of aqueous solutions of these materials were determined as prescribed by the ASTM (2). Normal behavior was observed by the derivatives of epoxidized butyl tallate with several of the materials showing equilibrium surface tension values of 35 to 40 dynes per centimeter (Fig. 2). The derivatives of epoxidized sperm oil (Fig. 3) and epoxidized methyl oleate (Fig. 4) showed a continuing linear decline of surface tension extending to a concentration of 0.10%. Interfacial tension of the solutions versus benzene showed a linear decline (Fig. 5–7). The water insoluble lower molecular weight derivatives were dissolved at the indicated concentrations in the

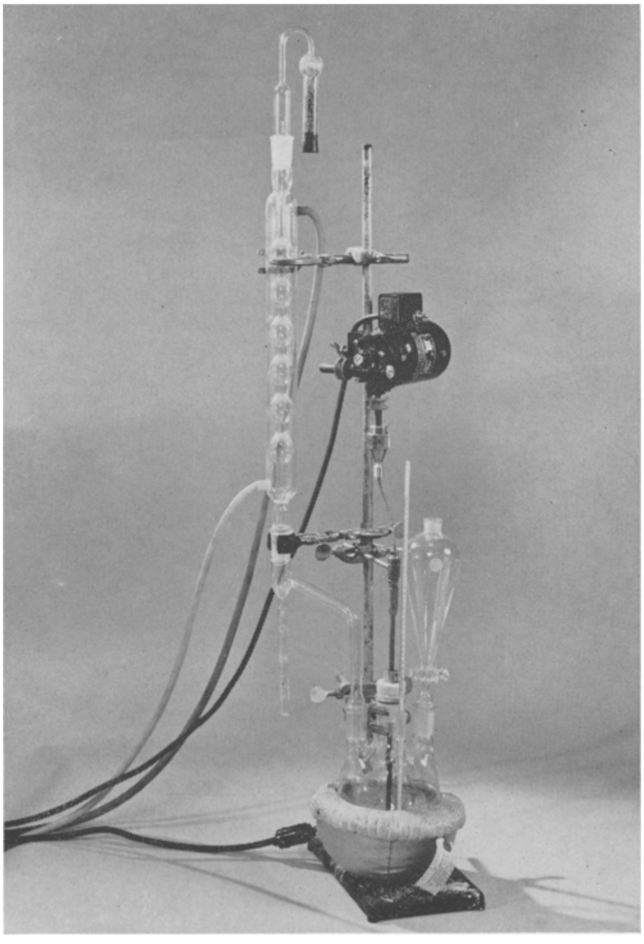

FIG. 1. Reaction vessel.

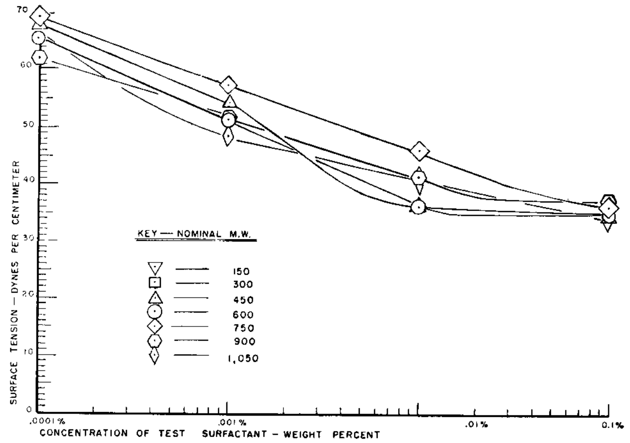

FIG. 2. Surface tension data—epoxidized butyl tallate derivatives.

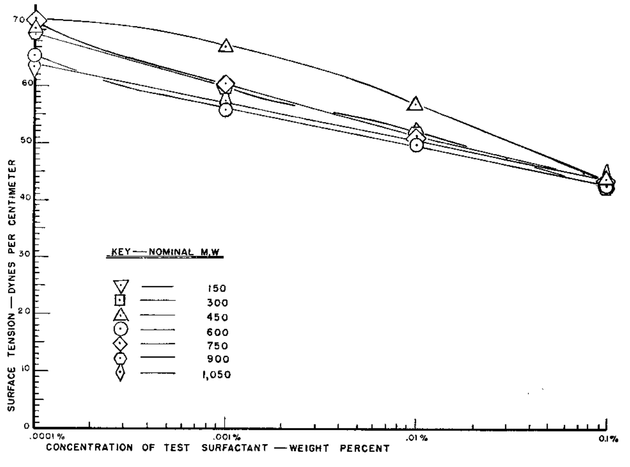

FIG. 3. Surface tension data—epoxidized sperm oil derivatives.

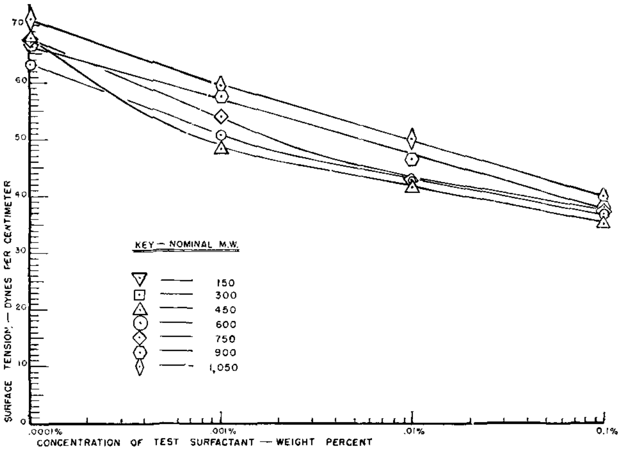

FIG. 4. Surface tension data—epoxidized methyl oleate derivatives.

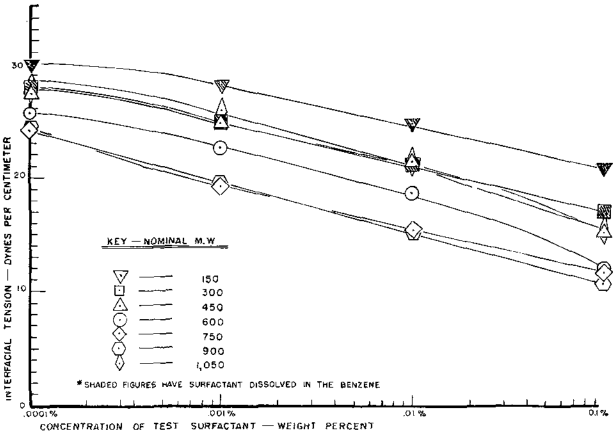

FIG. 5. Interfacial tension data—water solutions.

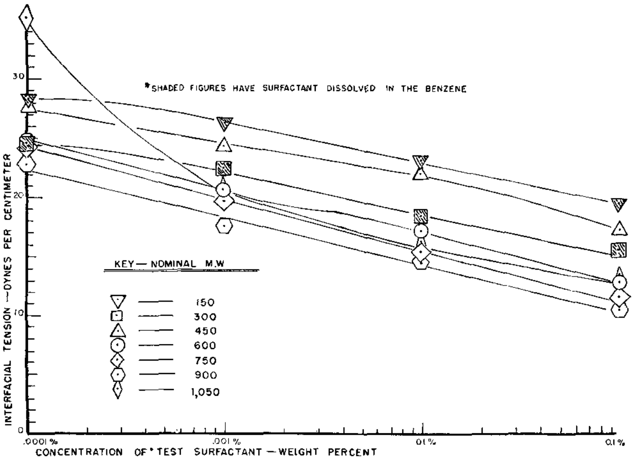

FIG. 6. Interfacial tension data—water solutions * vs. benzene-epoxidized sperm oil derivatives.

nonaqueous phase. Previous work (3) indicates that this gives valid data with derivatives of this type.

Interfacial tension of the solutions versus hexane (Fig. 8–10) showed rapid declines to values in some cases approaching 0 dynes per centimeter. Low interfacial tensions have been suggested by Ross (4) as being indicative of potential emulsification power when taking the interfacial and surface tension of the individual phases into account and computing spreading coefficients. This would seem to indicate that the materials could be potentially useful as emulsifiers for aliphatic hydrocarbons.

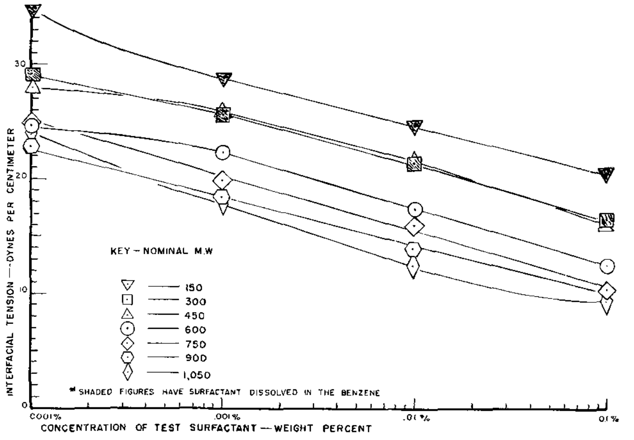

FIG. 7. Interfacial tension data—water solutions * vs. benzene-epoxidized methyl oleate derivatives.

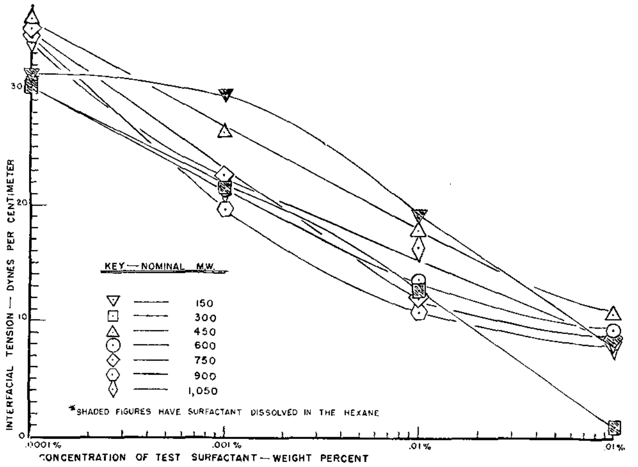

FIG. 8. Interfacial tenison data—water solutions * vs. hexane-epoxidized butyl tallate derivatives.

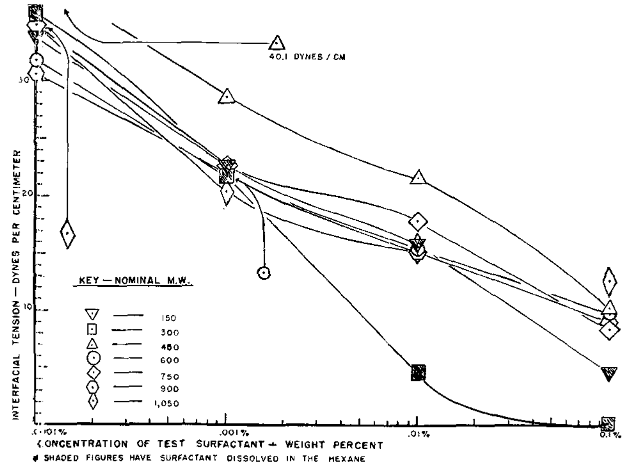

FIG. 9. Interfacial tension data—water solutions * vs. epoxidized sperm oil derivatives.

Foam

Pour foam data as originally suggested by Ross and Miles (5) were determined in accordance with the ASTM (6). Many derivatives of epoxidized butyl tallate (Fig. 11) and epoxidized methyl oleate (Fig. 12) showed moderate foam just after the solution had finished pouring. A 5-min standing period reduced all these values to 10 mm or less, indicating the foam was highly unstable. The foam height of the epoxi-

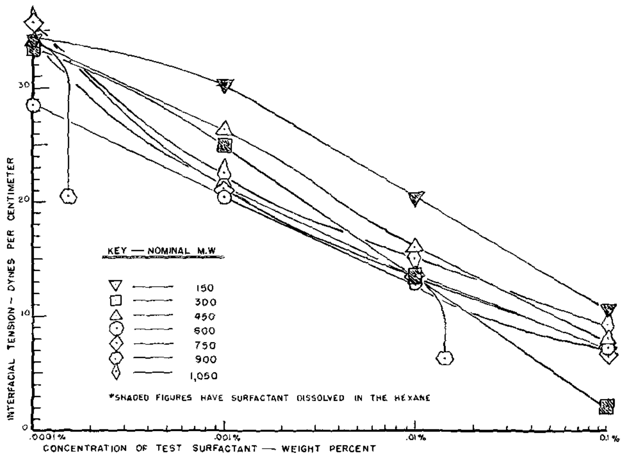

FIG. 10. Interfacial tension data—water solutions * vs. hexane-epoxidized methyl oleate derivatives.

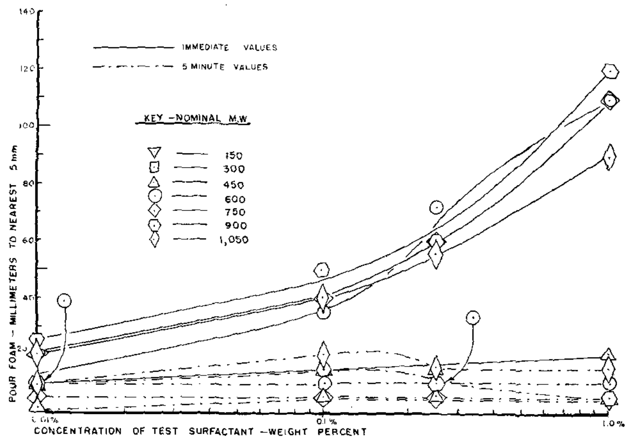

FIG. 11. Pour foam data—epoxidized butyl tallate derivatives.

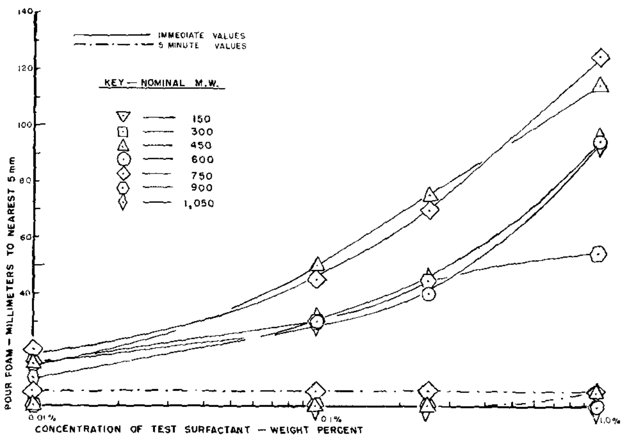

FIG. 12. Pour foam data—epoxidized methyl oleate derivatives.

dized sperm oil derivatives (Fig. 13) never did reach any appreciable value and what little foam there was was extremely unstable. This data suggests that these materials could possibly be used to effectively defoam other nonionic detergents.

Fabric Wetting

When evaluated in accordance with the AATCC (7) the derivatives of epoxidized sperm oil showed little measurable activity as fabric wetting agents. The epoxidized methyl oleate and epoxidized butyl tal-

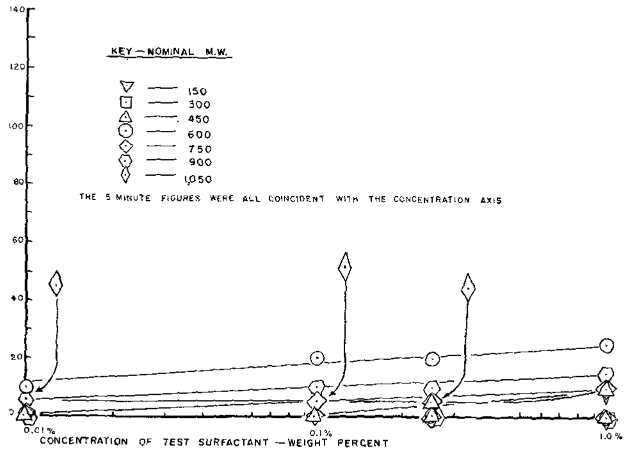

FIG. 13. Pour foam data—epoxidized sperm oil derivatives.

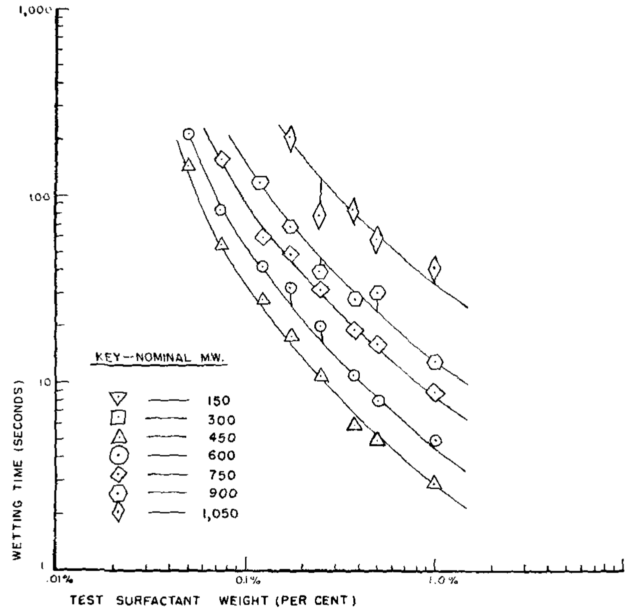

FIG. 14. Textile wetting time—epoxidized methyl oleate derivatives.

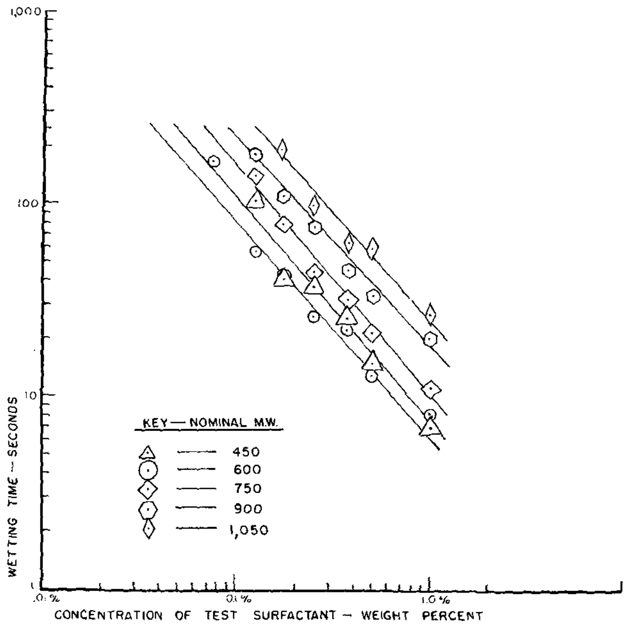

FIG. 15. Textile wetting time—epoxidized butyl tallate derivatives.

late derivatives both showed utility in this respect (Fig. 14 and 15). Generally speaking the fastest wetting times occurred with the materials having the lowest molecular weight, but a molecular weight (and HLB) sufficiently high to be soluble. These materials are the most hydrophobic in nature and are, therefore, those most actively seeking a surface upon which to exhaust themselves. The relatively fast wetting times of many of these derivatives indicates their possible use as wetting agents in textile treating. Much has also been attributed in the textile trade to the action of the ester group insofar as its function to lubricate the interfibril intrastices is concerned. These materials, having the ability inherent in a surfactant to penetrate yet the functionality of a sterically unhindered alkyl ester group, could easily have a significant application in this area.

The use of some classes of these materials as chemical intermediates for production of other surface active materials has been explored in a previous paper (8).

ACKNOWLEDGMENTS

Assistance and cooperation from W. P. Smith, D. G. Chapman, S. F. Hajac and S. J. Iwanicki.

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[Received October 29, 1964]