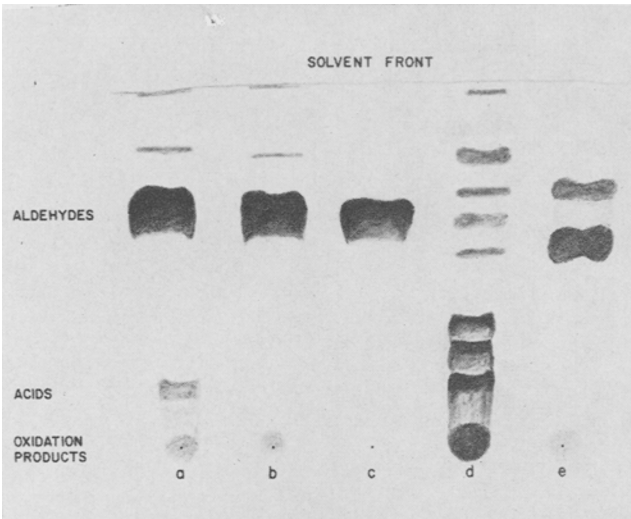

FIG. 3. Thin-layer silicic acid adsorption chromatogram of aldehydes.
Solvent system: 95:5 petroleum ether (b.p. 30–60°C.) -ethyl ether
Development time: 30 min.
Indicator: Iodine vapors
a) Crude linolenaldehyde containing fatty acids, b) undistilled linolenaldehyde, acid-free, c) distilled linolenaldehyde, d) pot residue from the distillation of linolenaldehyde showing products of thermal and oxidative decomposition, and e) undistilled aldehydes from menhaden oil, acid-free.

are only slightly segregated even by thin-layer chromatography, which gives more discrete separations than does column chromatography. Molecular distillation of crude linolenaldehyde improved the purity only slightly, as may be seen from the chromatogram shown in Figure 3b, c.

Methyl esters derived from menhaden oil exhibit subfractionation (Figure 1d) when chromatogrammed on thin layers of silicic acid (6). This phenomenon was observed in the present work with the acyloins and the aldehydes as well (Figures 1e, f; 3e).

Summary

The preparation of linolenaldehyde and of mixed aldehydes from highly unsaturated sources, such as menhaden oil *via* the acyloin condensation, is described. Reduction of the acyloins and subsequent cleavage of the glycols gave over-all yields of 85 to 90% free aldehydes.

The intermediates in the synthesis as well as the final products were analyzed in part by the novel method of thin-layer silicic acid chromatography.

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Sulfates of Ethoxylated Tridecyl Alcohol in Dishwashing Formulations[1]

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THE DEMAND for light-duty liquid detergents for household dishwashing has grown rapidly over the past few years. Present-day products are generally based on alkylaryl sulfonates, fortified with various auxiliary foam boosters. Sulfates of ethoxylated hydrophobes have found broad acceptance because of their ability to impart excellent foam stability to formulations, especially in the presence of greasy soil. In addition, they are relatively low in cost as compared with other competitive materials.

Earlier work in this field has been reported by Weil *et al.* (1), who investigated the performance of the sulfated ethoxylates of the tallow alcohols in the Ross-Miles foam test. These investigators also used a dishwashing test, based on the Terg-O-Tometer as developed by Leenerts (2), to measure the relative cleaning-power of a pure surfactant. They found that wetting time increased while foam height and the ability to clean dishes decreased with increasing ethylene oxide content.

Currently there are three important sources for sulfated ethoxylate derivatives. These are the alkylphenols, oxo-based tridecyl alcohol, and lauryl alcohol from fatty sources. The object of the work reported in this paper has been to compare the relative efficiencies of sulfated ethoxylates, in particular those based on tridecyl alcohol, as foam stabilizers in typical light-duty, liquid dishwashing formulations. The effect of both ethylene oxide to hydrophobe mole ratio and various sulfating agents has been established. Emphasis has been placed on a carefully controlled dishwashing procedure as the best available measure

[1] Presented at the fall meeting, American Oil Chemists' Society, Los Angeles, Calif., Sept. 28–30, 1959.

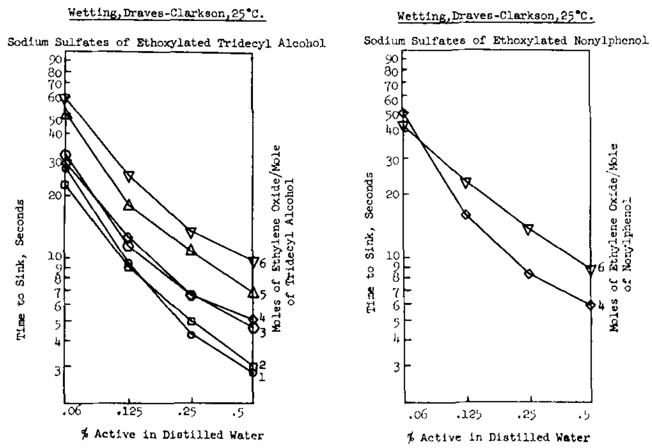


FIG. 1.

of performance for this type of surfactant application. To our knowledge precise, scientific measurements which directly correlate with actual household dishwashing performance have not been developed. In addition, the sulfated ethoxylate derivatives have been examined in the Ross-Miles foam test and the Draves-Clarkson wetting test.

Experimental Procedures

Preparation of Sulfated Ethoxylates. The ethylene oxide adducts used in this study were prepared in pilot-plant quantities by the Jefferson Chemical Company. The tridecyl alcohol, lauryl alcohol, and nonylphenol were ethoxylated in identical equipment to the desired ethylene oxide content. The adducts were then sulfated in our laboratories, using sulfur trioxide, sulfamic acid, and chlorosulfonic acid. The sulfation procedures employed (3) in our laboratories have been shown to give excellent yields with a minimum of side reactions. After neutralization the products were analyzed by cationic titration according to the method of House and Darragh (4) to determine the activity of the final product. On the basis of this analysis these materials were adjusted to the same activity prior to testing or formulating for dishwashing. Since there is some question about the precise ethylene oxide content in these adducts, no attempt was made to isolate or analyze for pure compounds.

Product Evaluation Tests. The sulfated ethoxylates were tested in the Ross-Miles foam test and the Draves-Clarkson wetting test as described by Harris (5). The ammonium salts of these materials were formulated with ammonium dodecylbenzene sulfonate, isopropyl alcohol, and water. Dishwashing evaluations were made according to the procedure developed in our laboratories (6). Reproducibility of duplicate determinations for this test is ±1 dish at the 95% confidence level. The standard soil consists of molten vegetable shortening weighed onto each plate and aged over-night. Initial foam is developed by directing a carefully controlled stream of water into the dishpan containing the concentrated detergent solution. Dishes are washed by hand under a carefully controlled time-cycle. The test is concluded when less than half the surface of the dishwater is covered by a thin film of foam.

Discussion

Wetting Properties. Both the ammonium and sodium salts of the sulfated ethoxylate derivatives were evaluated. For convenience only the data for the sodium salts are presented since both salts gave approximately the same results (Figure 1). The data indicate that the greater the ethylene oxide content of the tridecyl alcohol derivatives, the less efficient these materials are as wetting agents. This observation is consistent with that of Weil (1), who found the same trend for the sulfated tallow alcohol ethoxylates. Relatively small differences were noted between the tridecyl alcohol and nonylphenol derivatives in our study.

Foam Properties. The Ross-Miles foam tests were carried out in zero hardness water at 1 wt. % surfactant concentration. As shown in Table I, the initial

TABLE I
Ross-Miles Foam Test of Sulfated Ethoxylated Hydrophobes, 25°C., 1 Wt. % Surfactant, Distilled Water

Sulfated adduct	Moles ethylene oxide/mole hydrophobe	Initial foam ht., cm.	5-Minute foam ht., cm.
Ammonium salt–tridecyl alcohol	1	18.0	17.5
	2	18.0	17.5
	3	18.5	17.5
	4	18.0	15.5
	5	17.5	15.5
	6	17.5	11.0
Sodium salt–tridecyl alcohol	4	17.0	14.0
	5	16.5	16.0
	6	17.5	10.0
Ammonium salt–nonylphenol	4	16.5	16.0
	5	17.0	16.5
	6	16.0	15.5
Ammonium salt–lauryl alcohol	3	14.5	13.5

foam height was comparable for all the derivatives tested and did not vary significantly with the ethylene oxide mole ratio. Foam stability, in general, was quite good. This test, when used with pure surfactants, does not correlate with dishwashing tests on the same surfactants formulated with alkylaryl sulfonate. On the other hand, it is more likely that the relatively

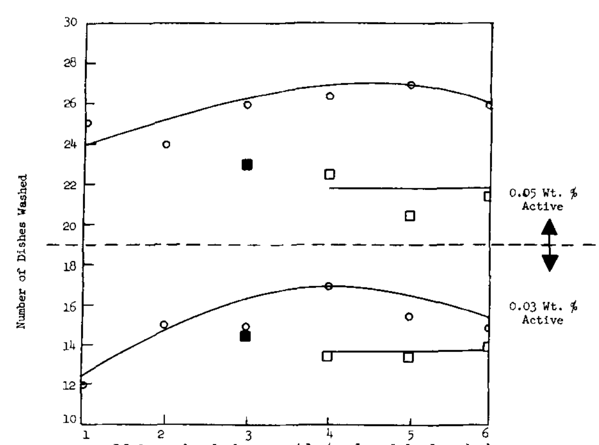
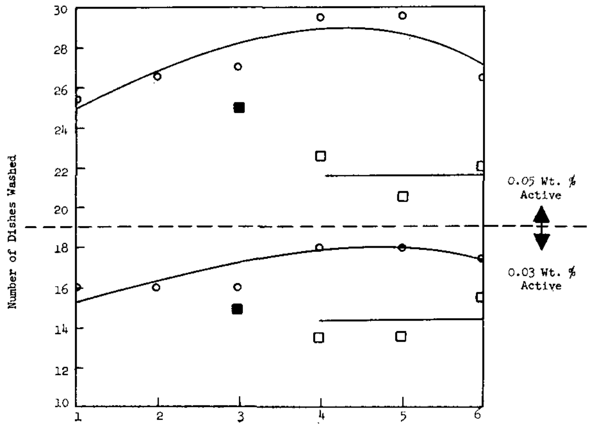


FIG. 2. Dishwashing foam-retention performance, ammonium salts of sulfated ethylene oxide adducts.

Water hardness: 135 p.p.m.

Formulation	Wt. %
Sulfated ethoxylate	15
Ammonium dodecylbenzene sulfonate	15
Isopropyl alcohol	20
Water	50

○ Tridecyl alcohol derivative
□ Nonylphenol derivative
■ Lauryl alcohol derivative
All sulfates prepared using chlorosulfonic acid.



• Moles of ethylene oxide/mole of hydrophobe.

FIG. 3. Dishwashing foam-retention performance, ammonium salts of sulfated ethylene oxide adducts.

Water hardness: 360 p.p.m.

Formulation	Wt. %
Sulfated ethoxylate	15
Ammonium dodecylbenzene sulfonate	15
Isopropyl alcohol	20
Water	50

○ Tridecyl alcohol derivative
□ Nonylphenol derivative
■ Lauryl alcohol derivative
All sulfates prepared using chlorosulfonic acid.

small diameter of the Ross-Miles tube supports even a transient foam for much longer periods of time than possible in a dishpan.

Dishwashing Characteristics. The sulfates of the one through six mole ethylene oxide adducts of tridecyl alcohol were compared with the corresponding four through six mole adducts of nonylphenol and the three mole adduct of lauryl alcohol in dishwashing tests. Various two and three active-component systems were investigated. All formulations were 30 wt. % active and contained 15 wt. % ammonium dodecylbenzene sulfonate.

An optimum in dishwashing performance was observed with the sulfate of the 4 to 5 mole ethylene oxide tridecyl alcohol adducts in binary systems. This optimum was independent of either water hardness or detergent concentration in the range tested (Figures 2 and 3). The sulfated tridecyl alcohol adducts were somewhat more effective in foam stabilization than the corresponding lauryl alcohol and nonylphenol derivatives. The sulfated 4 mole adducts, when tested at zero hardness, gave very poor foam stability (Table II). Collapse of the initial foam at this hardness level was almost instantaneous.

Although no quantitative measurements were made, qualitative observations indicated that the ability to remove grease in soft water continued long after collapse of the foam. Since the housewife judges the quality of a detergent by the stability of the foam, this aspect may not be significant to her.

TABLE II

Dishwashing Performance of Binary Systems at Various Water-Hardnesses, 4 Mole Adducts, 0.05 Wt. % Active

Sulfated ethoxylate of	Sulfating agent	Dishes washed			
		0 p.p.m.	35 p.p.m.	135 p.p.m.	360 p.p.m.
Tridecyl alcohol	$ClSO_3H$	4	22	27	29.5
Lauryl alcohol	$ClSO_3H$	4	22	23	25
Nonylphenol	$ClSO_3H$	....	....	22.5	22
Nonylphenol	NH_2SO_3H	2	25	26	27.5

Formulation	Wt. %
Sulfated ethoxylate (ammonium salt)	15
Ammonium dodecylbenzene sulfonate	15
Isopropyl alcohol	20
Water	50

As mentioned above, three-component systems were also investigated. For these studies total active concentration was again maintained at 30 wt. %, composed of 15% ammonium dodecylbenzene sulfonate, 7.5% sulfated ethoxylate, and 7.5% lauric diethanolamide or other ethoxylated derivatives. Invariably the addition of this third component increased the over-all performance over that of the corresponding binary system. This effect however was not uniform and depended upon both the type of added component and the water hardness.

A premium grade lauric diethanolamide was found to impart excellent soft-water performance to the formulations (Figure 4). A peak in performance occurs at about 35 p.p.m. hardness. Above this point the advantage for the alkanolamide formulation over the binary system diminishes and becomes relatively insignificant. A combination of ammonium dodecylbenzene sulfonate, lauric diethanolamide, and sulfated tridecyl alcohol ethoxylate (4-mole adduct) gave the best soft-water performance in this series.

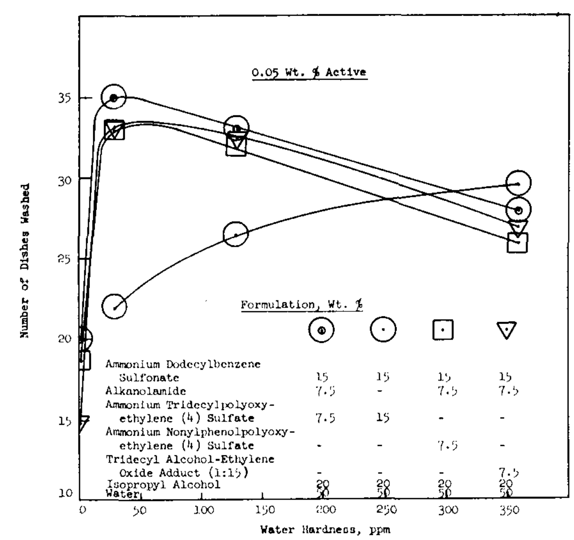


FIG. 4. Dishwashing foam-retention performance, influence of water hardness on formulations containing alkanolamide. All sulfates prepared by using chlorosulfonic acid.

Combinations of ethoxylated derivatives were also evaluated (Figure 5). The best performance was given by a formulation containing ammonium dodecylbenzene sulfonate and equal parts of the sulfated 4 mole adducts of nonylphenol and tridecyl alcohol. Although these ternary systems were equivalent to the binary system in zero and 360 p.p.m.-hardness water, they gave much better performance in intermediate hardness water.

In comparing all of the systems tested in this study, no one formulation was superior at all water hardness levels (Figure 6). Sulfated tridecyl alcohol ethoxylate (4 mole) in combination with lauric diethanolamide and dodecylbenzene sulfonate was the best formulation in soft water. On the other hand, above approximately 100 p.p.m.-hardness a ternary system also containing sulfated tridecyl alcohol ethoxylate (4 mole) with sulfated nonylphenol ethoxylate (4 mole) gave the best performance. In very hard water (360 p.p.m.)

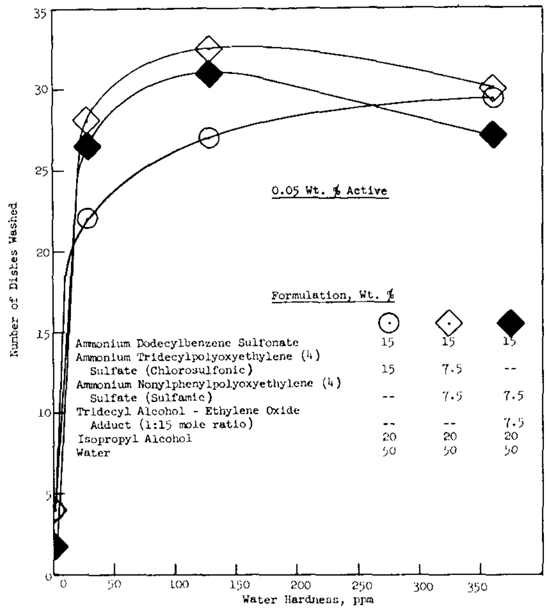


FIG. 5. Dishwashing foam-retention performance.

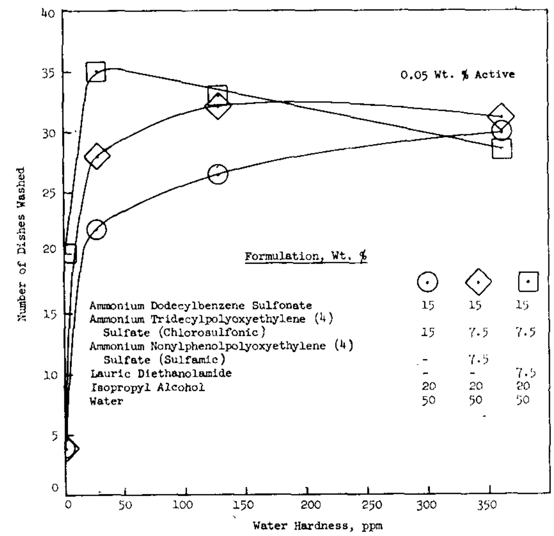


FIG. 6. Dishwashing foam-retention performance, influence of water hardness on binary and ternary systems.

the differences between all systems, including binary systems, were relatively small.

Effect of Sulfating Agent. Laboratory sulfations of the ethoxylated adducts of tridecyl alcohol, lauryl alcohol, and nonylphenol have been carried out with stabilized sulfur trioxide, chlorosulfonic acid, and sulfamic acid. Tridecyl alcohol ethoxylates give essentially quantitative yields of sulfate with sulfamic acid and 95–99% yields with the other sulfating agents. The poorest unbleached color is obtained with stabilized sulfur trioxide. The alcohol ethoxylates gave lighter-colored sulfates than the corresponding nonylphenol adducts.

Dishwashing performance of the sulfated alcohol ethoxylates was independent of the sulfating agent employed (Table III). On the other hand, the nonylphenol ethoxylates must be sulfated with sulfamic acid in order to achieve maximum performance and good color. This limitation should enable the manufacturer of sulfated alcohol ethoxylates to realize certain economies through use of the less costly sulfating agents.

TABLE III
Influence of Various Sulfating Agents on Foam Stability, Binary System, 4 Mole Adducts, 135 p.p.m.

Sulfated ethoxylate	Sulfating agent	Dishes washed 0.03% Active	Dishes washed 0.05% Active
Tridecyl alcohol	SO_3	16.5	27
Nonylphenol	SO_3	14.5	21
Tridecyl alcohol	$ClSO_3H$	16	26.5
Nonylphenol	$ClSO_3H$	13.5	22.5
Tridecyl alcohol	NH_2SO_3H	16.5	27.5
Nonylphenol	NH_2SO_3H	16	26

Formulation	Wt. %
Sulfated ethoxylate (ammonium salt)	15
Ammonium dodecylbenzene sulfonate	15
Isopropyl alcohol	20
Water	50

Summary

The foam stability of several light-duty liquid dishwashing formulations containing sulfated ethoxylates of tridecyl alcohol, lauryl alcohol, and nonylphenol have been compared. The effects of water hardness, sulfating agent, and ethylene oxide/hydrophobe mole ratio have been examined. In very soft water formulations containing alkanolamide and tridecyl alcohol derivatives were shown to be especially effective. At higher water-hardnesses, combinations containing sulfated ethoxylates of tridecyl alcohol and nonylphenol performed best. Optimum ethylene oxide content for the sulfated tridecyl alcohol ethoxylates has been shown to be 4 to 5 moles/mole of alcohol regardless of water hardness or detergent concentration. The alcohol ethoxylates were shown to be more tolerant of stronger sulfating agents with respect to product quality than the alkylphenol ethoxylates.

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