

Development of a Phosphate-Free Home Laundry Detergent¹

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ABSTRACT

A group of multifunctional surfactants was synthesized in order to arrive at materials which might function well in hard water. The salts of alkylaryl sulfopropionates, $R-C_6H_4-COCH_2COOCH_3$; alkyl-

aryl sulfonamides of taurine $R-C_6H_4-SO_2NHCH_2CH_2SO_3Na$; and the alkylaryl sulfonamide of aminoethylsulfuric acid $R-C_6H_4-SO_2NHCH_2CH_2OSO_3Na$ were found to be quite effective. These compounds were synthesized via conventional routes and their biodegradability was established. These materials were formulated into the detergents with the aid of various organic and inorganic builders other than condensed phosphates. The detergency of these materials was evaluated with the aid of standard test cloths. Analogously formulated detergents based upon linear alkylbenzenesulfonate were also included for comparison in this evaluation study. It was found that a number of fairly satisfactory phosphate-free heavy duty detergent formulations could be developed.

INTRODUCTION

Eutrophication of the Nation's lakes has become a problem causing great concern to government and industry. Combined with other factors, the phosphates of detergents as well as fertilizers can help to promote this eutrophication. Continued increase in the use of phosphate-containing detergents, due to elevated cleaning demands and an increase in the population, would magnify the problem. The development of phosphate-free home laundry detergents has thus assumed great significance.

The major functions of condensed phosphates in detergents can be summarized as follows: (a) chelation of calcium and magnesium ions; (b) lowering of the critical micelle concentration (cmc); (c) soil suspension by deflocculation; and (d) supply a reserve alkalinity at a buffered

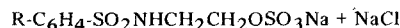
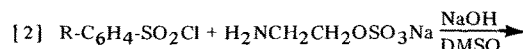
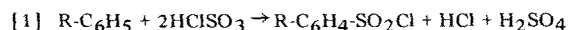
pH of 10-11. Though other benefits are claimed for the phosphates, the above four appear to be the most important ones. Since alkylbenzenesulfonates and fatty alcohol sulfates (the most popular anionic surfactants used in the U.S.) are adversely affected by calcium and magnesium ions, the hard water ion chelating function of phosphates allows for more efficient cleaning by these materials. Our work seeks to circumvent this problem by the use of surface active compounds which possess some self-chelating properties or which are less adversely affected by hard water.

The phosphate detergency functions of soil deflocculation, alkalinity and lowering of the cmc would be compensated for by the use of other organic or inorganic builders, or both. Conceivably the lowering of the cmc should be accomplished by the use of electrolytes such as carbonates, sulfates or chlorides. Soil suspension is normally achieved though the use of carboxymethylcellulose (CMC) and the elimination of the phosphate could be compensated for by a concentration increase in this component. The final phosphate function, that of alkalinity reserve, could be served by silicates, carbonates and other alkalis.

EXPERIMENTAL PROCEDURES

Synthesis of the Surfactants

The candidate surfactants are representative of two types of surface active agents which promised to be less affected by hard water ions. The first surfactant class is the sulfated and sulfonated sulfonamides, represented by sodium dodecylbenzenesulfonamidoethyl sulfate ($C_{12}H_{25}-C_6H_4-SO_2NHCH_2-CH_2OSO_3Na$) (1) and sodium dodecylbenzenesulfonamidoethyl sulfonate ($C_{12}H_{25}-C_6H_4-SO_2NHCH_2CH_2SO_3Na$). The synthetic route is shown as follows:



Surfactant 112A.

The second class of surfactants, alkylaroyl(sulfo)propionates, is represented by methyl 3-dodecylbenzoyl-3(2)-(sodium sulfonato)propionate ($C_{12}H_{25}-C_6H_4-COCH-(SO_3Na)CH_2CO_2CH_3$) (2).

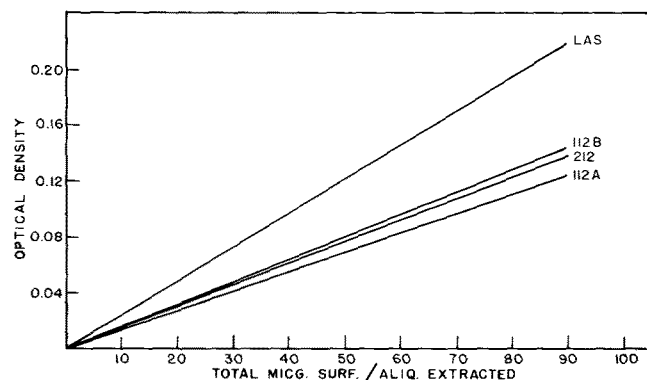


FIG. 1. Reference calibrations for surfactant-methylene blue complex.

TABLE I

Formulation code	Detergent Formulations, %				
	A	H	O	35	40
Surfactant	20.0	20.0	20.0	20.0	20.0
Cocodiethanolamide	2.0	2.0	2.0	2.0	2.0
Carboxymethylcellulose	2.0	2.0	2.0	2.0	2.0
Na silicate 1:2.4	10.1	10.1	8.4	10.1	10.1
Na acetate	---	---	20.0	20.0	20.0
Na citrate	---	---	---	17.0	20.0
NaCl	---	10.0	---	---	---
Na ₂ SO ₄	---	---	10.0	10.0	10.0
NTA	---	---	17.0	---	---

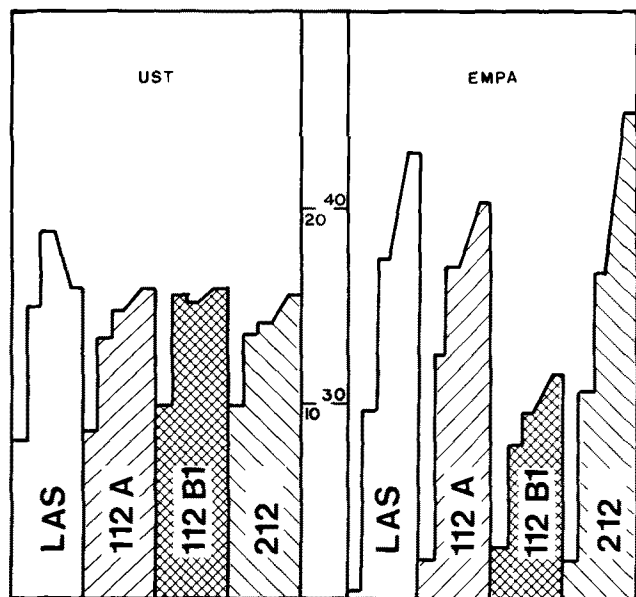
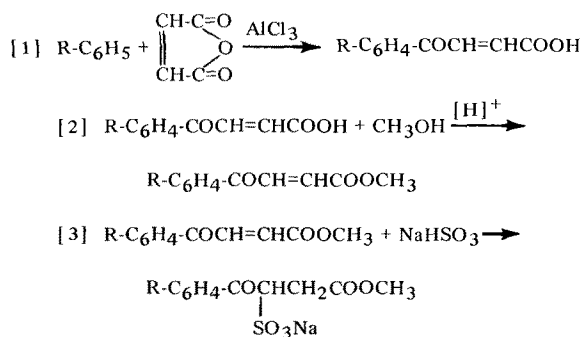


FIG. 2. Comparative detergency of four surfactants in soft water.



Surfactant 212.

Synthesis of Sulfated Sulfonamide Surfactant (112A)

In the experiment, 47.2 g dodecylbenzene (Continental Oil Nalkylene 500, mol. wt. 236) was dissolved in 50 ml dichloroethane. Then 51.3 g chlorosulfonic acid was added slowly at room temperature while cooling with an ice bath. The mass was then transferred to a separatory funnel and allowed to settle for 4 hr. The mass became cloudy after about 2 hr and a darker layer of spent sulfuric acid settled on the bottom. After 4 hr this bottom layer of 16 g was discarded. Next 27 g sodium hydroxide was dissolved in 125 ml water and the solution cooled to room temperature. Then 15 ml dimethylsulfoxide (DMSO) was added followed by 28 g aminoethyl hydrogen sulfate. After all or most of the latter had dissolved at room temperature the sulfonyl chloride solution was added slowly to this solution with good cooling with an ice or water bath in order to maintain the temperature at or below 25 C. Stirring was continued without further cooling. After about 2 hr the initially milky white reaction mass turned somewhat more translucent and yellowish and the viscosity of the mass increased substantially. The pH dropped rapidly to 8. Occasionally a pH drop to 5 would occur in which case a few pellets of solid sodium hydroxide were added to bring the pH back to 8-9. Stirring at room temperature was continued until no further pH drop was observed for at least 30 min. Then 10 ml dichloroethane and 30 ml isopropanol were added, whereupon the viscosity dropped substantially. The reaction mass was then heated to 60 C and placed in a separatory funnel. A lower aqueous layer amounting to 75-80 ml was drawn off and discarded. The top layer was placed in a rotary evaporator to remove the chlorinated solvent and some DMSO. A small part of the resulting gelatinous mass was

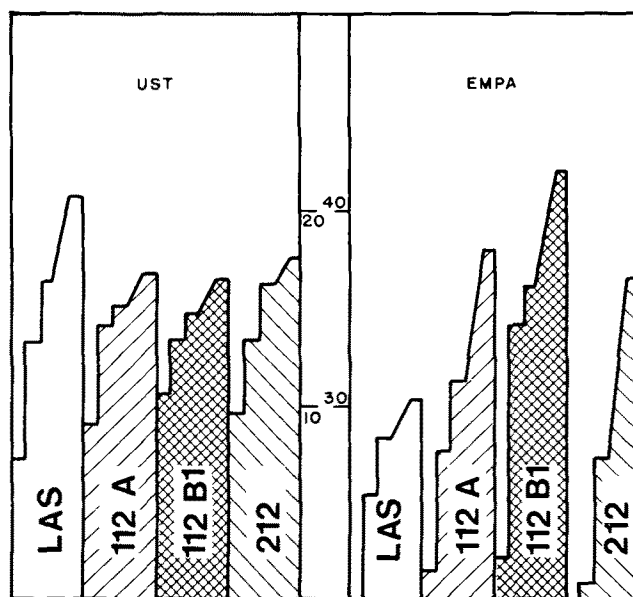


FIG. 3. Comparative detergency in medium hardness water.

dried further for NMR analysis. The remainder was dissolved in a mixture of 100 ml water and 30 ml isopropanol. A conversion of about 85±5% to the sulfonamide was obtained, the remainder of the titratable surfactant being LAS.

Synthesis of Sulfonated Sulfonamide Surfactant (112B)

Surfactant 112B was synthesized in exactly the same manner as above, except that 25 g of taurine was used in place of the aminoethyl hydrogen sulfate. In this case the conversion to the sulfonamide also amounted to 85±5%.

NMR Analytical Procedure

Proton magnetic resonance (PMR) proved to be a useful analytical aid to checking the conversion to sulfonamide contents of surfactants 112A and 112B. The method is based on area comparisons for all aromatic proton signals vs. the amide methylene proton signals. Theoretically the ratio of the two areas (four protons each) is 1.0 for both 112A and 112B. The major impurities contain an aromatic nucleus but no amide side chains; hence their presence is detected by a larger than theoretical aromatic proton area.

Dimethylsulfoxide-D₆ was the solvent of choice for PMR analyses. It dissolved all components in the final product (except for residual inorganic salts) and allowed good resolution of all spectral features.

Dodecylbenzenesulfonic acid or its sodium salt (linear alkylbenzenesulfonate [LAS]) could be formed either by incomplete reaction of chlorosulfonic acid and dodecylbenzene, or by competing hydrolysis of dodecylbenzenesulfonyl chloride during the Schotten-Baumann reaction. The sulfonyl chloride itself could be an impurity if this reaction did not go to completion. Didodecylbenzenesulfone could also be formed as a byproduct in the chlorosulfonation reaction. Obviously no differentiation or analysis of the final products could be attempted on the basis of the aromatic proton signals, as all four components have virtually identical PMR spectra in this region.

Other Schotten-Baumann reactants do not interfere with PMR analysis. The methylene protons of 2-aminoethyl hydrogen sulfate were readily distinguishable from those of the surfactants. 2-Aminoethanesulfonic acid (taurine) was not soluble in DMSO.

In practice a portion of the final product was stripped of all solvents and kept under vacuum with gentle heating (60 C) overnight. The product was shaken for 30 min with a portion of DMSO-D₆ insufficient to dissolve the entire

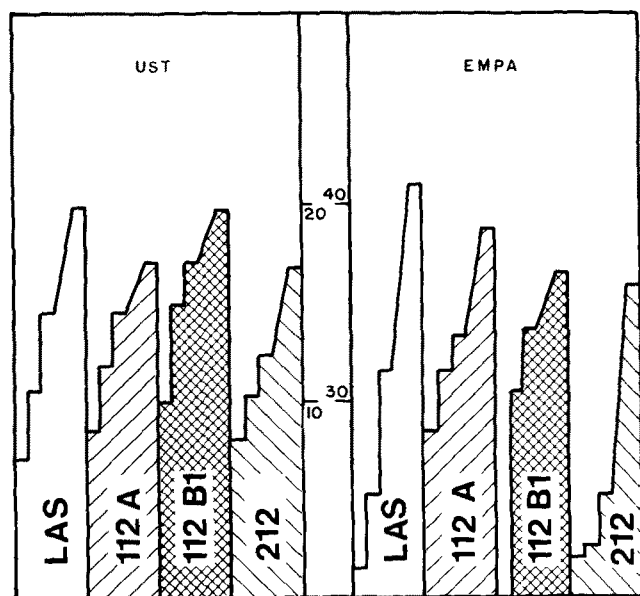


FIG. 4. Comparative detergency of four surfactants in hard water.

sample. The resulting solution was used for analysis.

Only the area under the low-field amide methylene group was measured. (The other methylene protons resonated too close to DMSO and the α -methylene protons *para* to the sulfonamido group for convenient area measurement.) This area was doubled and divided by the aromatic proton area to obtain the mole per cent of surfactant 112A or 112B in a particular sample. This calculation assumes that LAS was the predominant aromatic impurity, which was undoubtedly the case.

If the analysis were computed on the basis of didodecylbenzenesulfone as the sole impurity, there would be an upward revision in our reported assays, since there are eight aromatic protons per molecule of sulfone. There most likely is a small amount of sulfone present, along with LAS. Our assays are reported as $\pm 5\%$ to reflect the uncertainty in the impurities composition as well as inherent errors in spectrometer integration of proton areas.

Synthesis of Sulfopropionate Surfactant 212

The acrylic acid intermediate was prepared as follows: 49 g (0.5 M) maleic anhydride was mixed with 110 g dry dichloroethane in a three-neck flask equipped with a thermometer, magnetic stirrer, dropping funnel and a reflux condenser which was topped with a drying tube. The anhydrous aluminum chloride (120 g, 0.9 M) was added with cooling and, after 10 min of stirring, 118 g (0.5 M) of dried dodecylbenzene (Continental Oil Co., Nalkylene 500) was added slowly while maintaining the temperature at 20 C. After stirring at room temperature for 1 hr, the viscous dark brown mixture was poured into a beaker containing 450 g ice, 50 ml 66% sulfuric acid and 15 ml isopropyl alcohol. After thorough mixing the bright yellow mixture was allowed to stand and the upper layer was separated and washed twice with 70 ml portions of 66% sulfuric acid which contained 10 ml isopropyl alcohol. The unsaturated keto acid solution in dichloroethane was heated to 70 C to remove a water layer. For the purpose of IR and PMR spectra, the organic layer was stripped of solvent under reduced pressure, leaving a viscous amber liquid. Basic titration of this material required 2.75 meq/g. The theoretical value for the acrylic acid intermediate (b) is 2.91 meq/g.

The solution was then esterified with 19.2 g of methanol (0.6 M) and 5 ml concentrated sulfuric acid (or 2 g toluenesulfonic acid). The solution was heated at reflux for

.75 hr, the lower aqueous layer was separated and discarded, and an additional 12.8 g (0.4 M) methanol and 2 ml concentrated sulfuric acid (only of toluenesulfonic acid) were added. After refluxing for an additional 1.5 hr the organic layer was separated and the solvent was removed under reduced pressure. Titration of the residual oil with standardized ethanolic potassium hydroxide solution showed the acid content to be $<4\%$.

Conversion of the acrylate to the desired surfactant, 212, was accomplished by the addition of sodium bisulfite across the double bond. A Parr pressure reactor was charged with the ester and 52 g (0.5 M) sodium bisulfite in 140 ml water. The mixture was heated in the sealed container with stirring for 3 hr at 110-120 C. The yellow mixture was removed and dried in a vacuum oven at 55 C/13 torr. The anion content of this material was typically 2.01 meq/g as determined by cationic titration. The theoretical value for the surfactant is 2.23 meq/g, inferring ca. 90% purity.

Surfactant Biodegradability

The biodegradabilities of surfactants 112A, 112B and 212 were determined by the presumptive (shake culture) test (3). A commercial sample of LAS was included as a control.

Microorganisms were inoculated into flasks which contain a chemically defined microbial growth medium and the test surfactant. Aeration was accomplished by continuously shaking the flask. Biodegradation was determined by measuring the reduction in surfactant content during the 8 day test period. These samples were analyzed for anion content by the methylene blue method as described below. The average value obtained from the seventh and eighth day samples were used to compute biodegradability. The microbial inoculum was obtained from the Metropolitan Sanitary District of Greater Chicago. The surfactant sample size was 30 mg/liter of culture medium.

Because we processed the samples immediately, the use of formaldehyde in the samples was unnecessary.

The general analytical procedure was as follows: The test sample was mixed with a stock solution of methylene blue. After allowing sufficient time for salt formation (.5 hr) the acidified solution was extracted with aliquots of chloroform. The combined chloroform extract was washed with an aqueous wash solution followed by backwashing of the aqueous layer with chloroform. The chloroform backwashings were combined with the original chloroform extracts. Finally the chloroform solution was brought to volume (100 ml) after filtering through a pledget of glass wool.

A requisite for the use of this analytical procedure for anionic surfactants is that a straight line relationship between optical density and concentration at the wavelength of the analysis are obtained. The test surfactants 112A, 112B and 212 possessed this requisite relationship (Fig. 1).

It is of interest to note that the slopes of the calibration lines for the surfactants generally decreased with increasing molecular weights of the *anionic* species. The theoretical molecular weights of the anions are: LAS = 315, 112B = 422, 212 = 429 and 112A = 438. The wavelength of 652 $m\mu$ was checked for each species involved and was found to be an acceptable region for all. The results of the presumptive biodegradability test were as follows: LAS (2 samples) 91.8% and 89.2%, surfactant 112A 87.3%, surfactant 112B 86.0% and surfactant 212 85.5%.

Detergency Evaluations

The surfactants were incorporated into fairly simple test formulations with the aid of builders generally considered to be innocuous to the ecology, such as sodium silicate, acetate, chloride, sulfate or citrate. The trisodium salt of

TABLE II

A. Detergency Values (ΔR) at 50 ppm Water Hardness

Formulation	Cloth							
	UST, concentration, %				EMPA, concentration, %			
	0.1	0.2	0.3	0.5	0.1	0.2	0.3	0.5
BRAND	13.7	17.8	18.7	19.4	48.7	49.0	50.1	50.4
AHAM	11.6	14.4	16.0	17.1	40.3	40.2	39.9	40.1
A-LAS	8.0	14.8	18.7	16.3	20.4	29.6	37.4	43.1
A-112A	8.4	13.3	14.7	15.8	21.8	32.4	36.9	40.2
A-112B	9.5	15.1	15.0	15.5	22.7	28.0	29.5	31.6
A-212	9.7	13.6	14.0	15.0	21.6	30.7	36.9	44.9
H-LAS	7.9	18.6	18.0	15.1	24.2	35.0	39.6	38.3
H-112A	9.3	16.9	16.9	14.8	24.4	35.0	39.8	41.9
H-112B	9.8	15.7	14.8	14.0	24.4	31.0	35.3	37.6
H-212	12.2	18.2	18.6	16.5	23.2	31.5	37.5	42.8
O-LAS	10.6	16.5	16.3	15.4	39.2	41.7	40.8	40.4
O-112A	12.3	16.4	16.5	18.2	42.5	42.4	41.3	41.8
O-112B	10.6	15.5	15.0	15.4	43.3	39.9	41.1	43.0
O-212	11.6	16.1	15.8	16.9	31.0	43.5	47.5	46.2
35-112A	11.7	13.2	14.1	14.9	29.6	41.7	43.7	40.7
40-112B	6.8	9.2	11.3	14.8	31.9	38.9	38.0	42.7

B. Detergency Values (ΔR) at 135 ppm Water Hardness

Formulation	Cloth							
	UST, concentration, %				EMPA, concentration, %			
	0.1	0.2	0.3	0.5	0.1	0.2	0.3	0.5
BRAND	12.6	16.8	17.6	18.8	40.9	45.8	46.9	49.4
AHAM	8.9	14.2	15.5	16.8	38.6	40.8	40.5	40.6
A-LAS	6.8	13.2	16.3	21.5	15.1	25.4	28.4	40.3
A-112A	9.1	14.0	15.0	16.6	21.4	27.8	31.3	37.9
A-112B	10.6	13.4	14.5	16.5	19.2	24.7	26.9	28.8
A-212	9.6	13.3	16.1	17.3	14.1	21.9	27.3	36.6
H-LAS	8.2	18.8	20.6	19.1	17.9	24.9	32.2	40.4
H-112A	10.9	19.3	19.2	20.0	22.7	30.2	34.6	39.1
H-112B	10.7	17.0	18.7	18.5	20.9	27.7	31.4	36.6
H-212	9.7	16.7	19.6	20.8	15.3	23.1	31.2	39.2
O-LAS	11.0	11.9	15.9	19.8	22.4	32.2	37.2	44.0
O-112A	16.6	13.8	15.6	20.5	25.4	38.1	39.4	36.9
O-112B	14.8	11.0	16.2	18.5	21.1	33.4	38.1	41.9
O-212	12.5	10.6	15.5	17.7	24.5	38.0	38.2	37.5
35-112A	12.8	14.9	12.4	12.8	25.6	35.5	36.9	39.4
40-112B	13.2	9.6	9.6	12.3	22.2	32.3	34.7	38.6

C. Detergency Values (ΔR) at 300 ppm Water Hardness

Formulation	Cloth							
	UST, concentration, %				EMPA, concentration, %			
	0.1	0.2	0.3	0.5	0.1	0.2	0.3	0.5
BRAND	10.9	14.5	17.2	19.2	32.7	46.1	45.8	47.8
AHAM	10.0	10.8	13.8	16.4	24.0	35.0	35.9	35.2
A-LAS	7.1	10.5	14.4	20.5	13.1	15.3	21.6	31.1
A-112A	8.3	11.7	14.6	16.9	18.0	21.6	23.3	28.5
A-112B	9.9	15.0	17.0	19.6	18.3	20.6	23.6	26.4
A-212	8.0	10.2	12.1	16.6	12.2	12.7	15.5	26.0
H-LAS	7.6	15.3	18.8	21.5	14.6	21.0	27.4	38.0
H-112A	11.2	19.0	19.3	19.7	20.2	25.3	27.8	33.4
H-112B	10.5	18.2	19.2	19.7	20.3	24.1	28.4	38.8
H-212	9.4	15.1	18.0	19.7	11.9	15.7	19.6	29.9
O-LAS	9.8	18.4	14.7	15.3	19.3	27.4	31.9	37.4
O-112A	18.1	19.7	14.9	16.3	22.0	31.3	37.4	40.0
O-112B	16.4	19.4	13.8	14.8	18.4	25.1	29.7	39.3
O-212	10.0	19.4	16.3	14.9	25.7	35.4	36.7	35.7
35-112A	10.5	14.9	15.4	14.7	22.7	30.7	35.5	39.8
40-112B	11.0	10.2	10.7	13.7	25.1	32.6	35.8	41.7

nitrioltriacetic acid (NTA) was also used since its safety seemed assured at the time this work was carried out. All formulations were prepared from aqueous stock solutions which is the reason why the more water-soluble cocodiethanolamide foam stabilizer was used rather than the more conventional monoethanolamide. The composition of the formulations is shown in Table I. Water represents the difference between the total percentage of ingredients and

100%. LAS formulations were also prepared for purposes of comparison.

Unfortunately no generally accepted laboratory detergency procedure has as yet been developed. We restricted the present study to Tergotometer (U.S. Testing Co.) evaluations of commercially available soiled cotton cloths, namely, EMPA 101 (Testfabrics, Inc.) and U.S. Testing Co. cloths. The results should therefore be considered merely as

preliminary screens for cotton detergency only, rather than complete evaluations. We adopted two detergents as standards. The first one designated as BRAND was a widely sold commercial heavy duty granular detergent based upon a blend of anionic and some nonionic surfactants built with sodium tripolyphosphate. The second standard detergent was one supplied to us through the courtesy of the Association of Home Appliance Manufacturers. This material designated as AHAM was a tripolyphosphate built LAS formulation containing no brighteners.

Significant lot to lot differences for both the U.S. Testing Co. (UST) and the EMPA cloths presented a serious obstacle to the valid correlation of the detergency data so that some form of normalization or adjustment of the data was required to permit meaningful comparisons of results.

Several statistically valid normalization procedures were available and frequently used in analytical evaluations where certain data variability could be traced to the presence of one or more uncontrollable or nonuniform conditions in the analytical system. The specific technique used depends upon the nature of the data and the kind of nonuniform condition for which data adjustment is required. In our case this nonuniformity for which data adjustment was required appeared to be due to variations in the relative ease of removal of the soil from the cloth, which in turn was primarily a function of variations in the manufacture of the cloth. The variations in the results obtained with a standard detergent, such as AHAM or BRAND could be used as an index to the variability of the soiled cloth, since, all other things equal, the differences found with the standard must then represent the differences inherent in the cloth.

The methods described here yielded data adjustment which was well within the limitations imposed by the precision of the analytical procedure. In this normalization one set of control data was assumed as representing "base line" data and the remaining sets of control data were then adjusted relative to this base line. A normalization factor was then calculated for each lot of cloth by dividing the control values into the base line values thus:

$$\frac{\text{Base line value}}{\text{Control value (lot x)}} = K(\text{lot x})$$

Normalization of the test data was carried out by multiplying the test results by the applicable normalization factor. It was found that, due to a sensitivity of some cloth lots to both hardness as well as detergent concentration, best data adjustment was obtained by separately calculating the normalization factors for each concentration at each water hardness. The BRAND was chosen as the reference detergent, rather than AHAM, because the larger numerical detergency values obtained with it were inherently less affected by small errors in the method. All normalizations were done using the ΔR values, that is, the difference in the reflectance readings before and after washing of the cloth. The reflectance differences (ΔR) were tabulated in Table III. It should be noted that the evaluations were run at three water hardnesses 50, 135 and 300 ppm and at four detergent formulation concentrations 0.1, 0.2, 0.3 and 0.5% and were limited to cotton only.

RESULTS AND DISCUSSION

The three anionic surfactants derived from an alkylbenzene bore a certain structural relationship to LAS. However in their detergency behavior they did not perform like LAS, even though the latter was an impurity present in 112A and 112B. Formulation "A," which was a basic formulation containing only surfactant, foam stabilizer, CMC and silicate, served well to illustrate this point. Figures 2-4 show a graphic representation of the data in bar form. The four steps in each bar indicate the concentrations of .1, .2, .3 and .5%, respectively. It should be noted that the U.S. Testing cloth was not particularly sensitive to the different surfactants or to changes in hardness. The EMPA cloth on the other hand was sensitive both to the surfactant and hardness. Thus in Figure 2 it will be noted that surfactants 112A and 212 on the EMPA cloth at 50 ppm are equal or superior to LAS. At 135 ppm (Fig. 3) the three test surfactants are all superior to LAS. Because of the bifunctionality of the surfactant molecules we had anticipated this type of effect. However at 300 ppm (Fig. 3), all surfactants are overwhelmed by the hard water ions.

The test surfactants responded well to additional builders as is shown in Table II. On the U.S. Testing cloth, a number of formulations surpassed AHAM and were equal to the BRAND in performance. On the EMPA cloth, which admittedly discriminated better, we were not quite able to approach the performance of a phosphate built LAS. However in many instances the test data were fairly close as, i.e., in the case of the citrate built formulation No. 40 using surfactant 112B. Likewise formulation No. 35, which is also citrate built in conjunction with surfactant 112A, came fairly close to the AHAM detergent. As can be seen from the data in Table III, NTA, which was used in formulation "O," was a good detergent builder.

In summary, it appeared to us that on the basis of single wash tests on artificially soiled cloth, formulations based on the above three anionic surfactants could be developed which can approach the performance of a condensed phosphate built LAS.

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REFERENCES

1. Eaton, J.T., *Summaries of Papers, World Congress on Surface Active Agents*, No. 70, Paris, France, 1954.
2. Hedrick, G.W., W.M. Linfield and J.T. Eaton, *Ind. Eng. Chem.* 44:314 (1952).
3. The Subcommittee on Biodegradation Test Methods of the Soap and Detergent Association JAOCS 42:986 (1965); APHA, AWWA and WPCF, *Standard Methods for the Examination of Water and Waste Water*, Boyd Printing Co., Albany, New York, 1965, p. 297.
4. "Statistical Analysis in Chemistry and the Chemical Industry," John Wiley & Sons, Inc., New York, 1954.

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