Soap-Based Detergent Formulations: XIII. Formulations with Alpha-Olefin Sulfonates as Lime Soap Dispersants[1]

W.R. NOBLE and **W.M. LINFIELD,** Eastern Regional Research Center, ARS, USDA, Philadelphia, Pennsylvania 19118

ABSTRACT

Heavy duty household type detergents were formulated from tallow soap-AOS(α-olefin sulfonate)-builder combinations. Various commercial AOS samples were evaluated. These were derived either from closely fractionated α-olefins such as C_{14}, C_{16}, and C_{18} or from samples representing broader mol wt ranges such as C_{14}-C_{16} and C_{16}-C_{18}. The builders incorporated into these combinations were a sodium silicate ($Na_2O:SiO_2$ = 1:1.6), sodium tripolyphosphate, sodium citrate, sodium carbonate, and trisodium nitrilotriacetate. Detergency evaluations of 0.2% solutions in 300 ppm hard water (as $CaCO_3$) were determined with three commercial soiled cloths and by a multiwash test in which clean cloth was repeatedly soiled and washed. The relative proportions of soap, AOS, and builder were varied to obtain maximum detergency, and comparisons were made to other soap-LSDA(lime soap dispersing agents)-builder combinations as well as to a commercial high phosphate detergent used as a control. Detergency performance of soap-AOS combinations ranked just below that of the commercial high phosphate detergent control and below that of soap formulations containing sodium methyl α-sulfotallowate.

INTRODUCTION

In previous publications from this laboratory, the formulation of detergents consisting of tallow soap, lime soap dispersing agents (LSDA), and various builders was reported. Initially, a variety of anionic surfactants were evaluated as LSDA (1-8); later, the study was extended to include amphoteric surfactants (9,10). A number of compounds of both types with high lime soap dispersing capability were formulated with tallow soap and a glassy sodium silicate to give highly effective detergents. However, potential manufacture of such a soap-based detergent has been hampered by the lack of availability of a recommended LSDA at a sufficiently low price. For this reason, a comprehensive study of the more readily available α-olefin sulfonates (AOS) was undertaken.

[1]Presented at the AOCS meeting, Philadelphia, September 1974.

TABLE I

Effectiveness of Various Surfactants in a Soap-Based Formulation[a]

Surfactant	LSDR	Detergency (ΔR)[b] TF	EMPA	UST
LAS	40	1	20	3
C_{14}AOS[c]	38	4	26	5
C_{16}AOS[c]	27	11	37	7
C_{18}AOS[c]	25	11	38	7
C_{16}-C_{18}AOS[d]	27	-	-	-
TMS	9	17	33	10
TAM	5	20	38	11
TSB	3	23	37	13
Control detergent		25	40	11

[a]LSDR = lime soap dispersant requirement; TF = Testfabrics polyester-cotton (65:35) cloth with permanent press finish; EMPA = EMPA 101 cotton cloth; UST = U.S. Testing Co. cotton cloth; LAS = sodium linear alkylbenzenesulfonate; AOS = α-olefin sulfonate; TMS = sodium methyl α-sulfotallowate; TAM = sulfated N-(2-hydroxypropyl) tallowamide (sodium salt); TSB = 3-sulfopropyl-dimethyltallowylammonium hydroxide innersalt (tallow sulfobetaine).

[b]Detergency of a formulation consisting of 64% soap, 21% surfactant, 15% sodium silicate ($Na_2O:SiO_2$ = 1:1.6).

[c]Gulf Research and Development Co.

[d]Witco Chemical Co.

EXPERIMENTAL PROCEDURES

Materials

The soap used in this study was supplied by Armour-Dial Co. (Phoenix, AZ). The approximate composition was 79% tallow soap, 14% coconut soap, and 7% moisture. AOS was supplied by Gulf Research and Development Co. (Pittsburgh, PA) and by Witco Chemical Co. (New York, NY). The Gulf samples were sulfonates of pure C_{14}, C_{16}, and C_{18} α-olefins; the Witco sample was a sulfonate of a C_{16}-C_{18} range α-olefin. A single sample of a commercial detergent containing ca. 50% sodium tripolyphosphate was used as a control in this study as well as in all other papers of this series.

Sulfated N-(2-hydroxypropyl)tallowamide, sodium salt (TAM), was prepared by the method of Weil, Parris, and Stirton (11), and 3-sulfopropyl-dimethyltallowylammonium hydroxide innersalt (tallow sulfobetaine, TSB) was prepared by the method of Parris, Weil, and Linfield (9). Sodium methyl α-sulfotallowate (TMS) was obtained from Stepan Chemical Co. (Northfield, IL). BW silicate ($Na_2O:SiO_2$ ratio = 1:1.6) was supplied by Philadelphia Quartz Co. (King of Prussia, PA). Nitrilotriacetate, trisodium salt (NTA), was supplied by Hampshire Chemical Division of W.R. Grace & Co. (Nashua, NH). Sodium citrate, sodium tripolyphosphate (STPP), and sodium carbonate were standard laboratory reagents.

Test Methods

Lime soap dispersant requirement (LSDR) was determined by the Borghetty and Bergman procedure (12). All detergency determinations were conducted in a Tergotometer (U.S. Testing Co., Inc., Hoboken, NJ). Single wash tests were performed with three commercial soiled swatches: Testfabrics polyester-cotton (65:35) cloth with a permanent press finish (TF) and EMPA 101 cotton cloth (EMPA) were obtained from Testfabrics, Inc., Middlesex, NJ; another cotton cloth (UST) was obtained from U.S. Testing Co., Inc. (Hoboken, NJ). Fifteen 4 in. diameter swatches, five of each cloth type, were washed together with 2 g of a detergent formulation dissolved in 1 liter 300 ppm hard water (as $CaCO_3$) for 20 min at 110 cycles per min at 120 F. In a preliminary detergency test series, Gulf C_{14} AOS, C_{16} AOS, and C_{18} AOS were compared to LAS (sodium linear alkylbenzenesulfonate), TMS, TAM, and TSB in a detergent formulation consisting of 64% soap, 21% test surfactant, and 15% silicate solids ($Na_2O:SiO_2$ = 1:1.6). Detergency was measured as the increase in reflectance (ΔR) after washing. Reflectances were determined with a Neotec True-Color colorimeter. The results of this test series, along with the LSDR for the individual surfactants, are listed in Table I. The ΔR values reported are averages of ten readings—two for each swatch.

TABLE II

Detergency (ΔR) of Soap-AOS-Builder Combinations

	Soap:AOS[a] ratio																	
	100:0			80:20			60:40			40:60			20:80			0:100		
Percent builder added	TF[b]	EMPA[b]	UST[b]	TF	EMPA	UST	TF	EMPA	UST	TF	EMPA	UST	TF	EMPA	UST	TF	EMPA	UST
10% Sodium carbonate	-8	30	3	13	30	6	20	33	11	24	30	11	28	31	11	31	27	11
20% " "	6	29	8	6	29	6	15	34	10	21	31	11	24	31	10	30	30	11
30% " "	0	29	5	5	29	6	13	33	9	19	32	11	22	31	10	25	29	11
40% " "	1	27	5	4	27	5	11	32	9	16	35	11	18	31	12	21	31	12
10% Sodium nitrilotriacetate	-5	36	3	18	41	8	33	41	10	33	39	13	37	32	12	38	28	12
20% " "	12	43	8	17	44	9	25	46	12	31	44	13	34	38	12	35	33	12
30% " "	12	42	7	19	46	10	20	47	12	21	45	10	25	40	11	28	38	12
40% " "	13	44	10	19	44	11	21	45	11	20	45	11	21	40	11	23	42	11
10% Sodium citrate	-11	25	0	4	29	4	17	30	9	25	24	8	31	26	11	34	22	10
20% " "	-8	26	1	1	28	4	14	32	7	23	27	8	28	28	9	33	24	10
30% " "	-10	18	0	0	27	4	15	30	7	23	31	9	24	28	8	31	26	10
40% " "	-12	19	0	3	26	4	15	30	7	23	32	8	26	31	10	30	28	11
10% Sodium tripolyphosphate	-11	30	4	3	27	6	13	29	7	21	28	9	30	26	12	37	25	12
20% " "	-9	32	4	4	32	8	11	32	6	20	33	9	26	30	11	34	28	12
30% " "	0	32	5	7	33	8	13	40	7	17	38	9	24	35	11	28	33	12
40% " "	2	34	6	10	35	7	13	41	8	17	41	9	22	39	10	25	37	11
10% Sodium silicate[c]	0	32	2	15	43	9	22	32	11	25	25	12	21	25	10	27	19	12
20% " "	7	40	4	13	47	8	16	40	8	20	27	9	18	25	8	26	22	12
30% " "	7	39	4	9	38	6	15	37	7	17	29	7	20	22	9	27	24	12
40% " "	-4	27	1	8	31	4	13	28	6	18	26	7	18	22	8	25	25	12
Control detergent	27	42	13															

[a]Witco C_{16}-C_{18} α-olefin sulfonate.

[b]TF = Testfabrics polyester-cotton (65:35) cloth with permanent press finish; EMPA = EMPA 101 cotton cloth; UST = U.S. Testing Co. cotton cloth.

[c]$Na_2O:SiO_2$ = 1:1.6.

TABLE III

Grayness Buildup (-ΔR) Due to Soiling and Soil Redeposition after Six Successive Washes

	Formulation[a]		Grayness buildup (-ΔR)			
			Cotton		Polyester-cotton	
Soap	Surfactant	Builder	Soiling	Redeposition	Soiling	Redeposition
28%	42% AOS[b]	30% STPP	12.3	7.4	8.7	5.3
14	56	30% STPP	12.7	6.8	7.9	4.6
54	36	10% NTA	13.8	8.1	8.7	5.0
36	54	10% NTA	13.1	7.1	7.9	4.4
54	36	10% Sodium carbonate	12.2	6.8	8.7	4.8
28	42	30% Sodium citrate	12.5	7.2	7.7	5.2
54	36	10% Sodium silicate[c]	12.6	6.8	8.2	5.4
64	16% TSB	20% Sodium silicate[c]	10.1	5.1	5.5	2.5
Control detergent			13.4	9.9	9.4	7.6

[a]STPP = sodium tripolyphosphate; NTA = nitrilotriacetate (trisodium salt); TSB = 3-sulfopropyl-dimethyltallowylammonium hydroxide innersalt (tallow sulfobetaine).

[b]Witco C_{16}-C_{18} α-olefin sulfonate.

[c]$Na_2O:SiO_2$ = 1:1.6.

In another phase of this study, the single wash detergency of various ternary detergent formulations was determined. Here, different detergent builders were added at levels of 10, 20, 30, and 40% to binary formulations with soap:AOS ratios of 100:0, 80:20, 60:40, 40:60, 20:80, and 0:100. Witco C_{16}-C_{18} α-olefin sulfonate was used in this test series, and the results are shown in Table II.

Those formulations that performed well in single wash tests were further tested by the multiwash technique of Schwartz and Berch (13), in which grayness buildup was measured after six successive soilings and washings. Because the reflectance decreases due to dirt accumulation, grayness buildup is expressed as -ΔR. Two types of cloth were used: Testfabrics No. 400 80 x 80 bleached cotton print cloth and Testfabrics No. 7406 WRL polyester-cotton (65:35) with a permanent press finish. The test cloths were cut into 4 in. diameter swatches and washed twice in a Tergotometer with an 0.3% Calgon solution (in deionized water) to remove sizing. After the second wash, the swatches were rinsed thoroughly with deionized water. Before each washing step, seven cotton and seven polyester-cotton swatches per Tergotometer beaker were soiled with a suspension of 10 g of vacuum cleaner dirt from a Philadelphia office building in 1400 ml deionized water. Two unsoiled swatches of each type were washed along with the soiled swatches in order to measure soil redeposition. These swatches were not soiled but were washed six successive times along with the soiled test pieces. After six successive soilings and washings, the reflectance of the soiled and redeposition swatches was determined. The grayness buildup and soil redeposition data are shown in Table III.

RESULTS AND DISCUSSION

Previous studies have shown no direct correlation between LSDR and detergency of a soap-based formulation for surfactants with an LSDR range of 2-10. While efficient lime soap dispersing ability of a surfactant is a prerequisite for good detergency of a modified soap, a surfactant that shows exceptional detergency by itself appears to make also a considerable contribution to the detergency of the soap-based formulation. However, in a comparison of surfactants whose LSDR vary over a much wider range, a correlation of detergency with LSDR becomes evident, as shown in Table I. For example, LAS is the poorest lime soap dispersant among the surfactants listed in Table I. It is not a good detergent by itself, and thus it cannot be expected to perform well in a soap-based detergent. As the alkyl side chain of the AOS is increased from C_{14} to C_{16} and to C_{18}, the LSDR improves progressively, as does detergency, so that the AOS become increasingly effective as dispersants in soap-based formulations. An LSDR of 10 has been established empirically as an acceptable upper limit on the basis of previous studies, and the substantial improvement of detergency of the soap-based formulations with surfactants possessing LSDR below 10 is quite apparent in Table I. The exceptional effectiveness of amphoteric surfactants such as TSB is not only due to their very low LSDR and lack of antagonism to soap, but also to their excellent detergency by themselves when used in hard water.

The relatively high LSDR for AOS, as shown in Table I, suggested a need for an increase in the percentage of AOS in soap-based formulations if soap-AOS blends were to equal TMS, TAM, and TSB formulations in detergency. The data in Table II represent single wash tests of the three commercial soiled cloths for the following soap:AOS ratios—100:0, 80:20, 60:40, 40:60, 20:80, and 0:100; to each of these binary mixtures was added sodium carbonate, NTA, sodium citrate, sodium tripolyphosphate, or sodium silicate at 10, 20, 30, and 40% levels. The Witco C_{16}-C_{18} AOS sample was used in generating the data in Table II since it is more typical of commercial AOS samples currently available.

In general, the highest EMPA cotton detergency was obtained with a soap:AOS ratio of 60:40 regardless of choice of builder, whereas with the TF cotton-polyester blend a ratio of 20:80 or 0:100 was required for maximum detergency. The UST soiled cotton cloth was least sensitive to formulation changes, but here too the formulations containing more AOS than soap gave best performance.

An increasing amount of builder appeared to increase EMPA cotton detergency, whereas TF detergency is decreased with increasing amounts of builder. This behavior is typical for these two types of fabric, as was noted in an earlier publication (2).

From the above it can be seen that the selection of a soap-AOS-builder formulation possessing good detergency for all three types of soiled cloth involves a compromise.

By far the best builder in the single wash test was NTA. Formulations consisting of 60:40 soap:AOS or 40:60 soap:AOS and either 10 or 20% NTA were approximately equal to the control in cotton detergency and exceeded the TF detergency of the control. In general, the TF detergency was outstanding with this builder. When STPP was used as the builder, acceptable TF detergency was attained only with 40:60 and 20:80 soap:AOS ratios. Although not quite equal in detergency to that of the control, the 20:80 soap:AOS with 30% STPP represents a reasonable compromise with respect to the detergency of the three test cloths. The glassy sodium silicate, sodium carbonate, and sodium citrate were all about equal in performance but slightly poorer than STPP formulations. The silicate and sodium carbonate formulations gave acceptable detergencies with 60:40 soap:AOS and 10% added builder. The best compromise for sodium citrate formulations was 40:60 soap:AOS and 30% builder.

Eight of the formulations that performed well in single wash tests were also subjected to a multiwash test consisting of six successive soilings and washings. A commerical high phosphate built detergent was used as a control. A high performance soap-based detergent formulation was included for comparison purposes. This formulation consisted of 64% soap, 16% TSB, and 20% sodium silicate ($Na_2O:SiO_2$ = 1:1.6). All five builders listed in Table II were used in the AOS formulations so that there was at least one formulation incorporating each builder. The results are summarized in Table III. None of the AOS formulations had grayness buildup as low as those of the soap-TSB-silicate formulation. However, all AOS formulations were either equal to or slightly better than the control. While distinct differences in detergency due to builders could be observed in the single wash tests, no important differences could be detected in the multiwash test. A greater number of soilings and washings would probably be necessary to demonstrate any builder effects.

The data show that tallow soap can be formulated with AOS and a builder to give effective detergents. However, unlike the better lime soap dispersants, AOS must be used in substantially greater amounts to achieve good detergency.

REFERENCES

1. Bistline, R.G., Jr., W.R. Noble, J.K. Weil, and W.M. Linfield, JAOCS 49:63 (1972).
2. Noble, W.R., R.G. Bistline, Jr., and W.M. Linfield, Soap Cosmet. Chem. Spec. 48(7):38 (1972).
3. Parris, N., J.K. Weil, and W.M. Linfield, JAOCS 49:649 (1972).
4. Bistline, R.G., Jr., W.R. Noble, and W.M. Linfield, Ibid. 50:294 (1973).
5. Ibid. 51:126 (1974).
6. Marmer, W.N., D.E. VanHorn, and W.M. Linfield, Ibid. 51:174 (1974).
7. Micich, T.J., W.M. Linfield, and J.K. Weil, Ibid. 51:297 (1974).
8. Smith, F.D., J.K. Weil, and W.M. Linfield, Ibid. 51:435 (1974).
9. Parris, N., J.K. Weil, and W.M. Linfield, Ibid. 50:509 (1973).
10. Linfield, W.M., W.R. Noble, and N. Parris, Proc. 59th Midyear Meeting, Chicago, May 1973, Chem. Specialties Manufacturers Assoc., Inc., Washington, DC, p. 85.
11. Weil, J.K., N. Parris, and A.J. Stirton, JAOCS 47:91 (1970).
12. Borghetty, H.C., and C.A. Bergman, Ibid. 27:88 (1950).
13. Schwartz, A.M., and J. Berch, Soap Chem. Spec. 39(5):78 (1963).

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