Soap-Based Detergent Formulations: XX. The Physical and Chemical Nature of Lime Soap Dispersions[1]

J.K. WEIL, C.J. PIERCE, and W.M. LINFIELD, Eastern Regional Research Center,
ARS, USDA, Philadelphia, Pennsylvania 19118

ABSTRACT

Blends of soap and surfactants that possess good lime soap dispersing properties were dispersed in hard water. The turbidity of such dispersions varied depending on the type of dispersant used and also on the soap:dispersant ratio. Differences in coarseness of various dispersions could be measured empirically by filtration through a membrane of intermediate (1.2 μm) porosity. For determinations of the chemical composition of the dispersions a somewhat finer membrane (0.8 μm or less) was chosen, which retained most of the dispersed solids. Filter residues and filtrates were analyzed for sodium, calcium, magnesium and lime soap dispersing agents (LSDA). All of the calcium remained on the filter, whereas sodium was found primarily in the filtrate. Magnesium was held completely on the filter only if sufficient soap was present to tie up all Ca^{++} and Mg^{++}. Analysis of the organic portion of the residues indicated that the soap:LSDA ratio found was the same as that used in the preparation of the original dispersion. On filtration through a fine membrane (0.05 μm) virtually all dispersed material was retained on the membrane. The filtrate possessed only slight activity in terms of surface tension and detergency, whereas the resuspended solids possessed high surface activity similar to the unfiltered dispersion. This indicates that the dispersed solids are the major source of surface activity.

INTRODUCTION

It has been reported that the detergency performance of soap in hard water is substantially enhanced by the incorporation of certain surfactants that function as lime soap dispersing agents (LSDA) (1). It was also shown that lime soap dispersing ability and detergency enhancement are related to the chemical structure of the LSDA (2-4). Lime soap dispersing power and detergency improvement are not closely interrelated properties, as was shown in the case of nonionic surfactants, which are excellent LSDA but exhibit poor detergency in combination with soap (5).

On the basis of earlier work by Finkle et al. (6), Stirton and coworkers (7) proposed that stable lime soap dispersions were obtained with formulations of soap and those surface active agents which possessed a bulky terminal hydrophilic group and a long hydrophobic chain. The stable dispersions, accordingly, would consist of suspensions of particles in which soap and lime soap dispersing agent are intimately mixed rather than being suspensions of calcium soaps which are stabilized by surface adsorption of a small amount of LSDA.

The studied lime soap dispersions have a turbid appearance but are quite stable upon aging and do not precipitate (8). Repeated washing of fabric in such dispersions does not give rise to any substantial buildup of lime soap on the fabric (9); the effectiveness of a flameproofing finish on the fabric is not destroyed (10); and the detergency performance of the dispersions is usually equivalent to that of commercial phosphate-built detergents (8). On the other hand, washing with soap alone in water of equivalent hardness results in a substantial lime soap buildup on the fabric (9); flameproofing effectiveness is destroyed (11); and detergency is very poor (9).

The present study was undertaken to show that Stirton's view (7) of the soap-LSDA system was essentially correct. By analysis of the hard water dispersions of soap-LSDA combinations, which had been subjected to membrane filtration, it was shown that all of the LSDA, soap, and most hard water ions were contained in the filtered solids. It was also demonstrated that the filtered solids were the sole source of surface activity. Thus, soap does not act merely as a scavenger for divalent ions, and the surface activity is not due to the LSDA alone.

EXPERIMENTAL PROCEDURES

Materials

Sodium oleate was prepared from USP oleic acid by neutralization of its alcoholic solution with ACS grade sodium hydroxide. The dried soap was neutral to phenolphthalein and had the theoretically required sodium content. Samples of sodium oleate prepared in this manner are stable to oxidation even after a one year storage period at 0 C, as indicated by gas liquid chromatographic (GLC) analysis and lack of rancid odor.

The LSDA of this study were all laboratory preparations, and their syntheses are described elsewhere as indicated by references in Table I. For convenience the following abbreviations for the LSDA are used: PMS, sodium methyl α-sulfopalmitate, $C_{14}H_{29}CH(CO_2CH_3)SO_3Na$ (12); HSB, N-hexadecyl, N,N-dimethylammoniopropane 3-sulfobetaine, $C_{16}H_{33}\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$ (3); PASB, N-palmitamidopropyl, N,N-dimethylammoniopropane 3-sulfobetaine, $C_{15}H_{31}\text{-}CONHC_3H_6\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$ (3); and SAEO, oxyethylated N,N-bis(2-hydroxyethyl) stearamide $C_{17}H_{35}CON[(C_2H_4O)_xH](C_2H_4O)_yH$, where $x + y = 12$ (5).

Hard Water

Local tap water, which had a hardness of 210 to 230 ppm (as $CaCO_3$), was adjusted to 300 ppm with a 1000 ppm concentrate of a hardness composition of 32% Mg^{++}, 68% Ca^{++}. Water of 150 ppm hardness was prepared by dilution of this solution with dionized water. Water hardness was monitored regularly by EDTA titration and checked periodically by atomic adsorption spectroscopy.

Preparation of Dispersions

Two methods were used for the preparation of lime soap dispersions. Method A is less time consuming and corresponds more closely to laundry practice. Dry sodium oleate and lime soap dispersing agent were dissolved in 300 ppm hard water with vigorous agitation. Method B is somewhat slower but gives more reproducible turbidity data. Ingredients were dissolved in deionized water, and hard water concentrate was added to bring hardness to the required level. All preparations were initially warmed to about 60 C to speed dissolution of soap and LSDA, cooled to room temperature, and finally aged for at least one hr before measurements were made.

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TABLE I

Turbidity and Filtration Data for Various Lime Soap Dispersions

				Dispersions (.2% in 300 ppm water prepared by method B)		
Structure	Code[b]	Reference	LSDR[a]	LSDA:Soap *ratio*	*Turbidity*	Solids on 1.2 μm *filter in* g[c]
No LSDA				0:100	curd	0.163
$\underset{\downarrow}{C_{17}}H_{35}CON[(C_2H_4O)_xH][(C_2H_4O)_yH]$ x+y=8.4		5	9	5:95	curd	--
				10:90	0.45	--
				20:80	0.15	--
$\underset{\downarrow}{C_{17}}H_{35}CON[(C_2H_4O)_xH][(C_2H_4O)_yH]$ x+y=12	SAEO	5	3	5:95	0.58	--
				10:90	0.45	0.157
				20:80	0.12	0.141
$\underset{\downarrow}{C_{12}}H_{25}\overset{+}{N}(CH_3)_2C_3H_6SO_3$		3	4	5:95	0.38	--
				10:90	0.22	--
				20:80	0.17	--
$\underset{\downarrow}{C_{16}}H_{33}\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$	HSB	3	4	5:95	0.31	--
				10:90	0.09	0.135
				20:80	0.09	0.034
$\underset{\downarrow}{C_{15}}H_{31}CONHC_3H_6\overset{+}{N}(CH_3)_2C_3H_6SO_3^-$	PASB	3	2	5:95	0.33	--
				10:90	0.13	0.170
				20:80	0.13	0.03
$\underset{\downarrow}{C_{14}}H_{29}CH(COOCH_3)SO_3Na$	PMS	12	9	5:95	curd	--
				10:90	0.49	0.167
				20:80	0.23	0.127
$\underset{\downarrow}{C_{15}}H_{31}CONHC_2H_4OSO_3Na$		15	4	5:95	0.37	--
				10:90	0.31	--
				20:80	0.08	--
$\underset{\downarrow}{C_{16}}H_{33}OC_2H_4OSO_3Na$		16	3	5:95	0.69	--
				10:90	0.39	--
				20:80	0.11	--

[a] LSDR is grams of lime soap dispersing agent required to maintain a dispersion of the lime soap curd from 100 g of sodium oleate (14).

[b] See Experimental Procedures for explanations of abbreviations.

[c] From 100 ml dispersion.

Turbidity

A Fisher Electrophotometer II with a green filter was used to measure turbidity. Values at or below 0.5 absorbance per cm were measured in a 1 cm cell. For measurement of higher turbidities, an 0.8 cm spacer had to be inserted, and the readings were multiplied by a factor of 5. Turbidity values for dispersions prepared by Method B are shown in Table I.

Filtrations

All filtrations were carried out in cylindrical pressure filters of a 47 mm diameter. Membranes were supplied by Millipore Corp. (Bedford, MA). Pressure from a nitrogen line was varied from 2 to 30 lbs per sq in. depending on the porosity of the filter and nature of the dispersion. When the initial filtrate came through more cloudy than the main filtrate, the first few ml of the filtrate were recyled. Amounts removed were reproduced within 5% when filtrations were run under identical conditions.

Cation Analyses

Dispersions in 300 ppm and 150 ppm water hardness were prepared by Method A. One hundred ml of 0.2% dispersions were filtered through 0.8 μm porosity membranes. Both filtrates and filter residues were first oven dried and subsequently ashed in a muffle furnace at 750 C. The ashes were dissolved in 2 ml of 6N HCl and washed into a 50 ml volumetric flask. After appropriate dilution, calcium, magnesium, and sodium were determined with a Perkin-Elmer model 306 double beam atomic adsorption spectrophotometer. Final dilutions of calcium and magnesium solutions contained 1% lanthanum and 5% HCl to reduce ionization. Cation analyses are shown in Table II.

Anion Analyses

Method A was used in the preparation of dispersions. The dispersed solids from 400 ml of 0.2% dispersions of PMS-sodium oleate combination in 300 ppm hard water were filtered off on 0.8 μm porous membranes. Membranes with 0.22 μm porosity were used for the finer PASB-soap dispersions. The amount of PMS in the filter residues was calculated from the sulfur analyses of the residues. In addition, the amount of anionic surfactant in the filtrate was determined by methylene blue determination of the methylene blue active substances (MBAS) (13), and the amount of MBAS in the residues was calculated by differences. PASB in the filter residues was determined by elemental analyses for S and N. The results are summarized in Table III.

Surface Active Properties

Surface tension was measured by the Wilhelmy method with the aid of new glass slide covers, 1.82 cm x 1.84 cm x .0014 cm. Table IV lists surface tension measurements of filtrates from 0.2% dispersions of soap alone and 90% soap + 10% PASB in 300 ppm hard water. The dispersions were prepared by Method A. The filtrates were successively diluted with deionized water as shown in the table.

The Borghetty-Bergmann method (14) was used to measure lime soap dispersant requirement (LSDR) of the various surfactants used as shown in Table I.

For the purpose of detergency measurements, dispersions were prepared in the following manner. PASB (0.2 g) and 1.8 g of sodium oleate were dissolved together in one liter of hard water (300 ppm). A 500 ml portion of the dispersion passed through an 0.8 μm membrane while the remaining 500 ml portion was set aside unfiltered. A second one liter dispersion was prepared in an identical manner and

TABLE II

Cation Analysis[a]

			Filter residues removed by 0.8 μm membrane				Filtrate			
				Analysis, mg				Analysis, mg		
Composition[b]	Water hardness as $CaCO_3$ ppm	Turbidity before filtration absorbance/cm	Residue collected[c] mg	Ca	Mg	Na	Weight of filtrate[c] mg	Ca	Mg	Na
Soap only	300	3.7	166	6.8	2.1	0.0	34	0.2	0.1	10.1
10% PMS	150	0.8	126	3.1	1.0	1.5	94	0.2	0.4	15.0
10% PMS	300	2.8	155	6.5	2.3	0.3	52	0.4	0.4	13.5
20% PMS	300	2.4	148	6.5	1.2	0.3	76	0.0	0.8	11.2
10% HSB	300	1.4	147	7.8	2.0	0.1	76	0.7	0.1	8.2
20% HSB	300	1.1	176	6.6	0.9	0.6	43	0.2	1.2	11.8
10% PASB	150	0.2	23	0.8	0.2	0.9	191	2.7	1.1	14.1
10% PASB	300	1.5	181	7.9	1.4	0.2	63	0.2	0.4	10.5
20% PASB	300	1.8	178	8.0	0.9	0.2	59	0.2	1.1	9.8
20% SAEO	300	2.1	151	6.2	1.1	0.0	82	0.0	1.4	12.9

[a] From 100 ml of 0.2% dispersion.

[b] Lime soap dispersing agent (LSDA) code shown on Table I. See Experimental Procedures for explanation of abbreviations under Composition.

[c] Moisture-free basis.

TABLE III

Anion Analysis of Filter Residues[a,b]

	Based on sulfur		Based on nitrogen		Based on MBAS[c]			
LSDA[d] in soap-LSDA formulation	Sulfur found %	LSDA content %	Nitrogen found %	LSDA content %	MBAS in filtrate found, mg	MBAS in filter residue by difference, mg	Filter residue %	LSDA content %
10% PMS[a]	0.65	8[e]			14	26	269	10
20% PMS[a]	1.12	13[e]			25	55	287	19
10% PASB	0.62	9[f]	0.64[g]	11				
20% PASB	1.22	18[f]	1.10[g]	18				

[a] From .4 g solids in 200 ml 300 ppm hard water.

[b] PMS based dispersions collected on 0.8 μm porosity membrane. PASB-based dispersions collected on 0.22 μm membrane.

[c] Methylene blue active substance (13).

[d] Lime soap dispersing agent (LSDA) code shown in Table I. See Experimental Procedures for explanation of abbreviations.

[e] Based on 8.61% S in PMS.

[f] Based on 6.93% S in PASB.

[g] Based on 6.08% N in PASB.

TABLE IV

Test for Surface Activity of Membrane Filtrations of 0.2% Dispersions in 300 ppm Water

	Fraction removed on filter, %	Surface tension, dynes/cm Filtrate dilution ratio 1/10	1/100	1/1000	1/5000
Sodium oleate dispersion					
Unfiltered		25	34	44	71
0.8 µm filtrate	74		37	66	
0.05 µm filtrate	78	53	68		
90% soap + 10 PASB dispersion					
Unfiltered		24	26	39	49
0.80 µm filtrate	55	25	31	39	45
0.05 µm filtrate	74	33	65		

TABLE V

Detergency of Suspended Material and Filtrates
.9 g Na Oleate + .1 g PASB in 500 ml 300 ppm Hard Water

	Detergency, ΔR[a] TF	EMPA	UST
Filtration through 0.8 µm filter			
Unfiltered dispersion	10	12	9
filtrate	5	8	4
Resuspended solids	2	13	4
Water blank	-3	6	3
Filtration through 0.05 µm filter			
Unfiltered dispersion	14	16	8
filtrate	-3	6	1
Resuspended solids	2	14	3
Water blank	-3	8	3

[a] ΔR. Increase in reflectance after washing.

500 ml of the dispersion was passed through a membrane of 0.05 µm porosity. Each of the filter residues, which collected on the membranes, was resuspended in 500 ml deionized water, and the detergencies of these suspensions were compared with those of the two filtrates as well as with the unfiltered dispersions of the same age. A deionized water blank was also run.

Detergency was measured as the difference in reflectance (ΔR) before and after washing in a Tergotometer operated at 120 F, 110 cpm for 20 min. Three 4-in. circular swatches each of EMPA 101 cotton (Testfabrics Inc., Middlesex, NJ) (EMPA) and Testfabrics cotton-polyester blend with a permanent press finish (TF) and two swatches of U.S. Testing Co. (Hoboken, NJ) (UST) cotton were washed in each beaker. Results are shown in Table V.

DISCUSSION AND RESULTS

The turbidities of hard water dispersions of various LSDA soap ratios are shown in Table I. Also shown are the lime soap dispersant requirements (LSDR) of a variety of nonionic, anionic, and amphoteric LSDA. The dispersions used in this study were prepared by Method B because they were generally more reproducible than dispersions prepared by Method A. While there is no correlation between turbidity and LSDR, curd formation occurs, as expected, whenever the LSDA:soap ratio is at or below the LSDR of the dispersant. Since the LSDR is determined at a dispersion concentration of 0.08%, whereas the test dispersions of Table I were at a concentration of 0.2%, it would appear that lime soap dispersing ability is not concentration-depdendent. In all cases, turbidity decreased with increasing LSDA content of the dispersions, and the amphoteric LSDA gave somewhat lower turbidities than the anionic or nonionic LSDAs.

The turbidity studies indicated the particulate nature of the dispersions, and it was thus anticipated that the dispersed matter could be separated by filtration through a polymer membrane of suitable porosity. This approach, indeed, proved feasible, and the chemical nature of the filtered dispersed matter was established. Dispersions prepared with four LSDA coded SAEO, HSB, PASB, and PMS were studied in greater detail. Dispersions were filtered through a membrane of intermediate pore size (1.2 µm), and the amounts of residue retained on the filter are shown in the last column of Table I. It was generally observed that the amount of retained material decreased with increasing LSDA content and, here again, the amphoterics at the 20% level appeared to give the finest dispersions.

For the remainder of this study, Method A was used for the preparation of the dispersions because it was somewhat more convenient and also because it corresponds more closely to actual use conditions. Membranes of a porosity of 0.8 µm or less were found to hold back most of the dispersed material and were therefore used in the analytical studies summarized in Tables II and III. Turbidity as shown in Table II increased with greater water hardness and usually decreased with higher LSDA:soap ratio as stated above. PASB, which is one of the most efficient LSDA, gave an unusually fine dispersion at a 150 ppm water hardness so that only a comparatively small amount of dispersed material was filtered off on the membrane.

Table II clearly shows that at 300 ppm water hardness almost all of the calcium and a large portion of the magnesium are concentrated in the filter residue. As the LSDA:soap ratio is increased from 10:90 to 20:80, more of the magnesium is found in the filtrate. The LSDA:soap ratio appears to have only a slight influence on the calcium distribution. This indicates that calcium is held selectively in the filter residue. Sodium ions, on the other hand, are concentrated selectively in the filtrate.

The actual percentages of LSDA in the filter residue were determined by elemental analyses for S and N. In addition, the amount of PMS in the filter residue was determined as the difference between the theoretical methylene blue active substance (MBAS) in the original dispersion and the MBAS found in the filtrate. From these data the percent LSDA calculated in the filter residue was almost identical to the composition of the original dispersion. This indicates that the soap and LSDA are intimately combined in the dispersion which is presumably of a mixed micellar nature.

It was initially attempted to use membrane filtration as a suitable method for determining particle size distribution of the dispersed material. However, it was found that filtration through a stack of membranes of successively decreasing pore size gave irreproducible results probably due to clogging of the membrane pores. Nevertheless, we were able to obtain some notion of particle size of the two dispersions by the quantity of residue retained by each membrane filter (Table IV). Seventy-four percent of all soap dispersion was retained by the 0.8 µm filter, while only 55% of the LSDA-soap mixture was held by that size filter. Approximately half of the LSDA-soap dispersion not retained on the 0.8 μm membrane was filtered out by the 0.05 μm membrane. A 1:10 dilution of the 0.05 μm filtrate of straight soap showed only slight lowering of the surface tension of water. The unfiltered soap dispersion, on the other hand, produced surface tension lowering even at a dilution of 1:1000 with deionized water. The dispersion of the soap-PASB mixture was also held back on the 0.05 μm pore size membrane with only a small amount of surface active material in the filtrate so that a 1:100 dilution did not show lowering of the surface tension. The unfiltered soap-PASB dispersion shows surface tension depression even at a dilution of 1:5000. Filtration of the all soap dispersion through a coarser membrane of a porosity of 0.8 μm indicates that the surface active material is again retained by the filter, whereas in the case of the soap-PASB dispersion a greater amount of material runs through the filter membrane. Thus, surface activity is shown even upon a 1:5000 dilution with deionized water. This indicates that the soap-PASB dispersion is much finer than that of the soap alone and shows that the more finely dispersed particles are the source of surface activity.

This thesis was also borne out by another series of experiments, the results of which are summarized in Table V. Here the detergency properties of the unfiltered whole dispersions were compared with those of the filtrates and of the filter residues redispersed in deionized water. The detergency tests of the 0.8 μm porosity filtration series and those of the 0.05 μm porosity series were run several weeks apart; thus there is a discrepancy between the data for unfiltered dispersions and blanks of the two test series. The data show that the filtrate through the 0.05 μm porosity membrane washed as poorly as that of the water blank. However, the filtrate from the 0.8 μm filter which, as was shown above, permits some surface active material to run through, showed a significant improvement over the water blank on TF cloth.

The redispersed filter residues were about equal in detergency on EMPA to that of the unfiltered whole dispersion. The TF detergency of the redispersed filter residues was significantly greater than that of the water blank but less than that of the filtrate.

The experimental evidence thus indicates that:

(a) The LSDA:soap ratio of the filtered solids is the same as that employed in the preparation of the original dispersion for different types of LSDA.

(b) When an approximately stoichiometric ratio of hardness ions and soap was employed, all of the calcium and part of the magnesium was found in the filtered solids, and most of the sodium was in the filtrate.

(c) Reaction of hard water ions with the LSDA:soap mixture did not destroy surface activity as it does with soap alone. Thus, the filtrate passing through an 0.05 μm membrane possessed essentially no surface activity while the filter residue upon redispersion in water was capable of washing fabric.

(d) The hard water ions do not react selectively with the soap and do not leave behind a solution of LSDA as the principal detergent.

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