Soap-Based Detergent Formulations: X. Nature of Detergent Deposits[1]

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ABSTRACT

The cumulative deposition of detergent residue on unsoiled cotton and polyester-cotton permanent press finish cloth was determined for a variety of detergent formulations after washing 25 consecutive times in 300 ppm hard water in a laboratory Tergotometer. Included in this study were: a phosphate-built laundry detergent, two carbonate-built detergents, tallow soap and various tallow soap formulations with anionic and amphoteric lime soap dispersing agents, and a glassy sodium silicate. Sample swatches washed with each formulation were analyzed for calcium, magnesium, and organic acid content. Fabric washed with the carbonate detergents showed the highest calcium and magnesium content, while those washed with the phosphate detergent and the soap-lime soap dispersant-builder formulations had the lowest. Fabric washed with soap alone had a much higher fatty acid residue than those washed with the other detergent formulations. However, the amount of organic acids left on the fabric after washing with a soap-lime soap dispersing agent formulation was no greater than that produced by phosphate- and carbonate-built detergents. The presence or absence of deposits also was verified visually with a scanning electron microscope. Each formulation also was tested for detergency by measuring the soil buildup in a multiwash procedure. Generally, the buildup of soil paralleled the deposit of detergent residue on the unsoiled cloths.

INTRODUCTION

Heavy duty detergents based upon combinations of tallow soap with lime soap dispersants and builders have been studied in this laboratory (1,2); a variety of anionic and amphoteric surfactants has been shown to function effectively as lime soap dispersants in such formulations (3-6). In these studies, performance evaluations were, for the most part, confined to single wash detergency tests. It generally is recognized that a multiple wash and soil methodology, such as the one developed by Schwartz and Berch (7), is more meaningful, since it takes into consideration the successive buildup of organic or inorganic deposits originating from either the soil or the detergent. This buildup is almost always detrimental to the cleaning process, as well as to the proper functioning of flame retardant finishes (8,9). Such deposits also can alter the feel or hand of the washed fabric. Successive buildup of inorganic salts, such as calcium or magnesium carbonate, will result in a harsh or boardy hand, while the buildup of hard water soaps leads to a greasy feel. Pacheco, and Carfagno, (9) investigated buildup caused by interaction of hard water with carbonate detergents and soap. Both types of deposits resulted in loss of effectiveness of the flame retardant finish, whereas a phosphate-built detergent neither gave rise to deposits on the fabric nor interfered with flameproofing.

It is thus desirable that a laundry detergent should not give rise to any appreciable deposits on the washed fabric. The present study was undertaken to determine the magnitude of deposits which might result from repeated washings in hard water with soap-lime soap dispersing agent (LSDA) formulations and to determine the chemical nature of such deposits. The effects of the soap-LSDA formulations upon flameproofing finishes are reported elsewhere (10). In this study, the buildup of deposits on washed fabric was followed analytically, as well as visually, with the aid of scanning electron microscope.

The present study is limited to four types of LSDA whose structures are as follows: $RCH(SO_3Na)COOCH_3$ (TMS), $RCONHCH_2CH(CH_3)OSO_3Na$ (TAM), $RCONHCH_2CH_2CH_2N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$ (TASB), and $RN^+(CH_3)_2CH_2CH_2CH_2SO_3^-$ (TSB), where R is a tallow-derived long chain alkyl group. The code names for the four lime soap dispersants will be used throughout this paper.

EXPERIMENTAL PROCEDURES

Materials

TMS was obtained from the Stepan Chemical Co., Northfield, Ill., as a 37% active paste under the name of Bioterge TMS. TAM was synthesized according to the procedure of Weil, et al., (11) and TSB was synthesized according to the procedure of Parris, et al. (6). TASB was prepared in the following manner (5): to 1200 g (1.40 mole) melted whole tallow, 460 g (4.49 mole) N,N-dimethyl-1,3-propanediamine was added with stirring. The reaction flask was stoppered and allowed to stand at room temperature for 2 days at which time ca. 90 mole percent amide was indicated by IR absorbance. One liter 1,2-dichloroethane was added to the amide after the unreacted diamine had been removed by distillation for 6 hr at 65 C and 0.15 mm Hg. The reaction mass was heated to 50 C, and 524 g (4.29 mole) propanesultone (since propanesultone is known to cause burns and cancer in animals, proper care must be exercised in handling this material.) was added dropwise over a 1 hr period with cooling to maintain the temperature at ca. 50 C. Thereafter, the mixture was kept at 50 C for 1 hr. Since the product precipitated as an amorphous lumpy mass, heat had to be applied to keep the reaction mass fluid. The solvent was removed in a vacuum oven, leaving behind a slightly tacky, solid product which was used for detergency testing without purification. The by-product glycerine was not removed.

The local tapwater in Wyndmoor, Pa., (210-240 ppm as $CaCO_3$) was adjusted to 300 ppm water hardness by addition of suitable quantities of calcium chloride and magnesium chloride in a mole ratio of 60:40 calculated as calcium carbonate.

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TABLE I

Composition of Detergents

Code no.	Detergent formulation composition[a,b]
1	Commercial phosphate detergent control
2	Commercial carbonate detergent A control
3	Commercial carbonate detergent B control
4	64% Soap + 21% TMS + 15% sodium silicate[c]
5	64% Soap + 21% TAM + 15% sodium silicate[c]
6	64% Soap + 16% TASB + 20% sodium silicate[c]
7	45% Soap + 11% TASB + 14% sodium silicate[c] + 30% sodium sulfate
8	64% Soap + 16% TSB + 20% sodium silicate[c]
9	45% Soap + 11% TSB + 14% sodium silicate[c] + 30% sodium sulfate
10	100% Tallow soap

[a]Formulations 4-9 contain 1% carboxymethylcellulose.

[b]TMS = $RCH(SO_3Na)COOCH_3$, TAM = $RCONHCH_2CH(CH_3)\ OSO_3Na$, TASB = $RCONHCH_2CH_2CH_2N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$, and TSB = $RN^+(CH_3)_2CH_2CH_2CH_2SO_3^-$, where R is a tallow-derived long chain alkyl group.

[c]$Na_2O:SiO_2$ ratio is 1:1.6.

TABLE II

Analysis of Deposits after 25 Consecutive Washings in Hard Water (300 ppm)

	Cotton			Polyester-cotton		
Detergent no.	Ca^{++} (%)	Mg^{++} (%)	Organic acid (%)[a]	Ca^{++} (%)	Mg^{++} (%)	Organic acid (%)[a]
1	0.04	0.01	0.2	0.04	0.00	0.2
2	5.61	0.39	0.2	3.52	0.09	0.2
3	1.90	0.23	0.2	0.76	0.24	0.2
4	0.05	0.02	0.2	0.56	0.00	0.2
5	0.05	0.02	0.2	0.04	0.00	0.1
6	0.06	0.02	0.1	0.04	0.00	0.3
7	0.20	0.06	0.2	0.05	0.03	0.2
8	0.06	0.02	0.1	0.05	0.00	0.2
9	0.05	0.03	0.1	0.04	0.01	0.1
10	0.13	0.01	1.5	0.33	0.01	0.7
Unwashed cloth	0.002	0.001	0.1	0.002	0.001	0.1

[a]Calculated as tallow fatty acid.

Fabric Deposit Studies by 25 Successive Wash Technique

Two types of cloths were used in the 25 repetitive wash experiments, namely: Testfabrics no. 400 W 80 x 80 bleached cotton print cloth and Testfabrics polyester-cotton (63/35) with a permanent press finish (the white portion trimmed from the standard soiled cloth).

Before use, the cloths were washed twice in a Tergometer with Calgon solution (3 g/liter deionized water). After the second wash, they were rinsed thoroughly with deionized water. Unless otherwise indicated, all washing tests were carried out in 1 liter 0.2% detergent in 300 ppm hard water (as $CaCO_3$) at 120 F for 20 min, followed by a 10 min rinse in 1 liter 300 ppm hard water at 120 F in a Tergotometer. One set of cloths, consisting of 9 test pieces of each of the 2 types of cloths, was washed 25 consecutive times with each detergent formulation to determine the amount of deposit buildup due to interaction between the detergent and water hardness.

Six soap-LSDA-builder formulations, three commercial control detergents, and a soap control were subjected to the 25 repetitive wash test. The composition of the detergents is shown in Table I.

Fabric Analyses

The fabric samples were analyzed after 25 successive washes. Organic residues were removed from one of the test pieces by Soxhlet extraction with 95% ethanol. After evaporation of the alcohol, the residue was taken up in 100 ml petroleum ether and 100 ml water containing 1 ml concentrated HCl. The organic layer was washed until free of mineral acid, the solvent was evaporated, and the residue was titrated with standard base in neutral alcohol. Fabric samples weighing 0.7-1 g were ashed at 750 C. The ash was dissolved in 2 ml constant boiling hydrochloric acid, and calcium and magnesium were determined on appropriately diluted solutions with an atomic absorption flame spectrophotometer. The analytical results are shown in Table II.

Scanning Electron Microscopy

The laundered test cloths were sampled by cutting with scissors into pieces ca. 6 mm x 6 mm. Pieces were attached to stubs by a thin layer of silver paint. Specimens were made conductive with ca. 15 nm gold-palladium alloy (60/40) on the rotary tilting stage of a Devton high vacuum evaporator and were observed in a JSM-50A scanning electron microscope at 8-10 KV, with an objective aperture of 200 μ. The scanning electron micrographs, Figures 1-4, show views of cotton and polyester-cotton test pieces after 25 successive launderings in detergents 1, 2, 4, and 10, respectively.

Schwartz and Berch Multiwash Detergency Tests

Washing performance of the 10 detergent formulations was determined according to the multiwash technique developed by Schwartz and Berch (7) in which grayness buildup ($-\Delta R$) was measured after 6 successive soilings and washings. Grayness buildup is determined as the difference in light reflectance measured with a Neotec Tru-Color colorimeter before and after washing. Since the reflectance decreases after washing, the grayness buildup is expressed as $-\Delta R$. The two types of cloths used in this test series were the same as those used in the 25 repetitive wash study above, and the washing conditions were as described above. Before each washing step, seven cotton and seven polyester-cotton swatches/Tergotometer bucket were soiled with a suspension of vacuum cleaner dirt in water. Two

TABLE III

Analysis of Fabrics after Six Soilings and Washings with 0.2% Detergent

	$-\Delta R$				
	Soiled	Redeposition	Organic acid (%)	Ca^{++} (%)	Mg^{++} (%)
Cotton					
Detergent no.					
1	9.3	6.0	<0.2	0.04	0.01
2	13.7	8.6	<0.2	0.22	0.02
3	8.3	5.3	<0.2	0.08	0.02
4	8.9	5.3	<0.2	0.03	0.01
5	9.5	6.3	<0.2	0.03	0.01
6	9.0	4.8	<0.2	0.02	0.01
7	9.7	5.3	0.2	0.03	0.01
8	7.9	4.1	<0.2	0.03	0.01
9	9.4	4.6	<0.2	0.03	0.01
10	23.9	9.8	1.6	0.11	0.01
Untreated cloth	0.0	0.0	<0.2	<0.01	<0.01
Polyester-cotton					
Detergent no.					
1	5.9	4.2	<0.2	0.03	0.01
2	8.5	6.5	<0.2	0.16	0.01
3	5.5	3.5	<0.2	0.06	0.01
4	5.8	4.0	<0.2	0.02	0.01
5	5.3	3.7	<0.2	0.02	<0.01
6	5.5	3.2	0.2	0.02	<0.01
7	7.6	4.5	<0.2	0.02	0.01
8	4.1	2.2	<0.2	0.02	<0.01
9	6.0	3.8	<0.2	0.02	<0.01
10	27.6	15.8	3.3	0.21	0.02
Untreated cloth	0.0	0.0	<0.2	<0.01	<0.01

unsoiled swatches of each type were washed along with the soiled swatches to measure redeposition ($-\Delta R$). After six soilings and washings, the reflectance of the soiled and redeposition swatches was determined. The grayness build-up and soil redeposition data are shown in Table III. In addition, organic acid and calcium and magnesium ion analyses were carried out on these fabric samples as described above. The analytical results are summarized in Table III.

RESULTS AND DISCUSSION

The development of soap-LSDA-silicate formulations shown in Table I was given in previous publications (1,2,5). The function of the sodium sulfate in formulations 7 and 9 is that of an inexpensive filler.

The data for the soap-LSDA-builder detergents, as well as for three commercial control detergents and a soap control, are shown in Table II. All of the soap-LSDA based formulations (detergents nos. 4-9) gave a buildup of calcium, magnesium, and organic acid ca. equivalent to that obtained after washing with a 50% sodium tripolyphosphate containing control detergent of commercial origin (detergent no. 1). The reasons for the somewhat higher calcium and magnesium contents of cotton washed in detergent no. 7 are not understood clearly. Very large calcium and magnesium deposits were found in fabrics washed in the commercial phosphate-free control detergents A and B (detergents nos. 2 and 3), both of which contained sodium carbonate as a builder. Among the detergents tested, only the soap control (detergent no. 10), besides showing slightly elevated calcium and magnesium assays, gave rise to a high fatty acid deposit. It should be noted that, in the organic acid determinations, a minimum titration (0.05 ml) corresponded to 0.15% organic acid (calculated as oleic acid) for an 0.8 g fabric test piece. Thus, acid content data of 0.15% or less in Table II have no significance. The data show clearly that washing with the soap-LSDA-silicate formulations does not cause any significant deposit formation on either cotton or polyester-cotton fabric after 25 successive launderings.

The above observations were confirmed qualitatively by

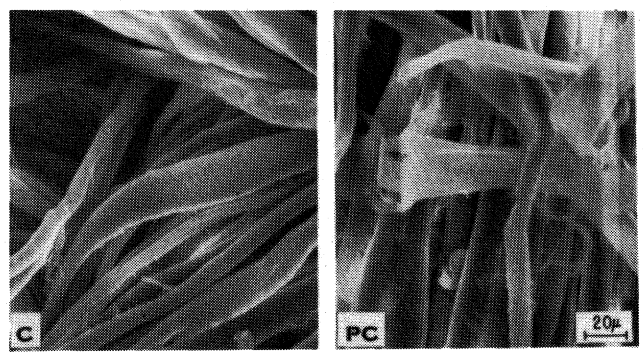

FIG. 1. Phosphate detergent. C = cotton and PC = polyester-cotton.

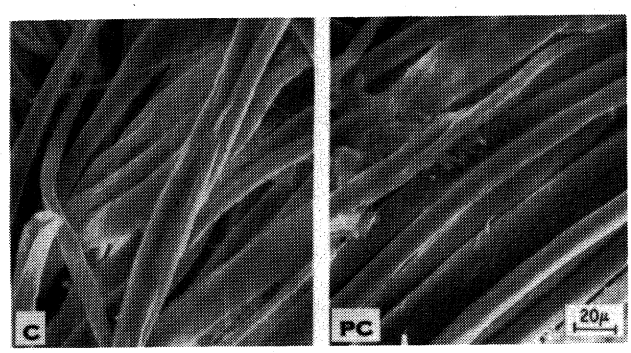

FIG. 2. Soap-based detergent no. 4. C = cotton and PC = polyester-cotton.

scanning electron microscopy. Four examples are reproduced here (Figs. 1-4). The phosphate-built control detergent no. 1 (Fig. 1), as well as all of the soap-LSDA formulations of which detergent no. 4 is a typical example (Fig. 2), shows no discernible deposits. Detergent no. 2 which was heavily built with sodium carbonate showed a typical calcium carbonate incrustation spread fairly evenly over the individual fibers of the fabric (Fig. 3). Detergent no. 3, a commercial carbonate-built nonionic detergent

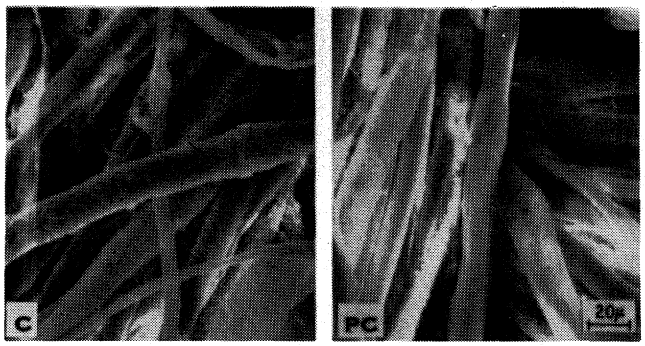

FIG. 3. Carbonate detergent. C = cotton and PC = polyester-cotton.

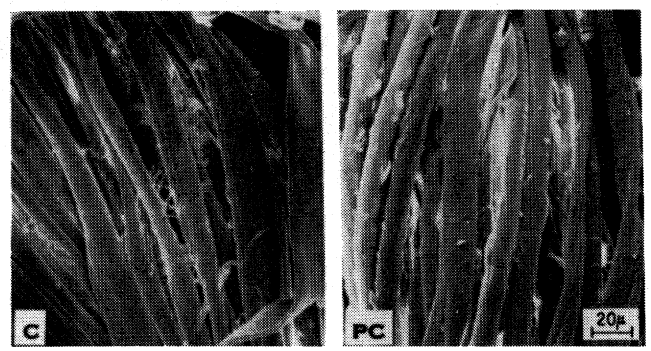

FIG. 4. Soap. C = cotton and PC = polyester-cotton.

showed the same phenomenon. Soap alone (detergent no. 10) produced clumps of matter randomly scattered over the fiber surface (Fig. 4). The same phenomenon also had been observed by Pacheco and Carfagno (9). As seen in the data in Table II, cotton is subject to more deposit than the polyester-cotton blend, particularly after washing in carbonate-built detergents (detergents nos. 2 and 3). Such differences, however, were not apparent in the scanning electron micrographs.

The effect of soil upon deposit buildup is shown in Table III. Test pieces obtained from the multiwash detergency test of Schwartz and Berch (7) were analyzed for grayness buildup, redeposition, and deposits. Although this multiwash technique involved only 6 successive launderings, the deposit buildups were substantial, and the results parallel those obtained from the 25 wash tests without soiling. The data show correlation between grayness buildup, soil redeposition, and amount of deposit on the fabric. The carbonate built detergent A (detergent no. 2) and soap alone (detergent no. 10) show the greatest amount of grayness buildup, soil redeposition, and calcium buildup and, of course, a high fatty acid buildup for soap alone. All of the soap-LSDA-builder formulations (detergents nos. 4-9) performed as well as the phosphate-built detergent no. 1 with respect to grayness buildup and redeposition and accumulation of deposits on the fabric.

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