Reduction of Phosphate Builder in Tallow-Based Detergent Formulations[1]

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ABSTRACT

Laboratory washing tests using two different kinds of standard soiled cotton were made to compare built solutions of hydrogenated tallow alcohol sulfate (HTAS), sodium methyl α-sulfotallowate (NaMeαST) and linear alkylbenzenesulfonate (LAS) in hard water of 300 ppm at 60 C. Most of the experiments were at 0.25% total concentration (0.05% active ingredient plus 0.20% builder). Phosphate reduction, without loss in detergency, can be accomplished in some cases but not in others, depending both upon the detergent and the test cloth. Both cloths have shown with HTAS as the active ingredient, that reduction in phosphate builder is possible without loss in detergency. The effect of other changes in formulation has been determined.

INTRODUCTION

The alkylbenzenesulfonates, the "work horse of the synthetic detergent industry," were at first known primarily as textile assistants, wetting agents, emulsifying agents, and the like. They did not become household detergents until the importance of the inorganic phosphate builders, particularly the tripolyphosphates and pyrophosphates, was established (1).

The function of the phosphate builders is not completely understood. They act as sequestering agents for the Ca^{++} and Mg^{++} of hard water, although the relation does not appear to be strictly stoichiometrical. They act as a source of buffered alkalinity and affect the micellar properties of the detergent. Further, they are able to remove soil to some extent and may have some desirable colloidal properties of their own to contribute to the washing process.

A packaged household detergent may contain about 20% active ingredient (AI) and 80% builder and fillers in the form of inorganic phosphates, borates, carbonates, silicates and sulfates. The phosphate content of 15 different solid packaged heavy duty household detergents now on the market (2) ranges from 22% to 36%, expressed as P_2O_5, with an average of 27%. A formulation listed (3) for a typical heavy duty solid detergent contains 18% AI and 50% sodium tripolyphosphate with a phosphate content of 29% and a P_2O_5/AI ratio of 1:6.

In agreement with the above the detergent formulation used in the present experiments, and also in previous investigations, comprised 20% AI, 44% $Na_5P_3O_{10}$, 8% $Na_2P_4O_7$, 8% Na_2SiO_3, 19% Na_2SO_4 and 1% carboxymethylcellulose (4-6). This amounts to 30% phosphate, as P_2O_5, and a P_2O_5/AI ratio of 1:5.

A survey of water hardness in rural and urban United States (7) has shown that 90% of the population would be satisfied with a detergent performing satisfactorily in water of up to 250 ppm. Most of our experiments were in hard water of 300 ppm which may therefore be considered a sufficient degree of water hardness.

The purpose of the present work was to observe the effect of reducing the usual amount of phosphate builder, in detergent systems in which the active ingredient was hydrogenated tallow alcohol sulfate (HTAS), sodium methyl α-sulfotallowate (NaMeαST), or linear alkylbenzenesulfonate (LAS). The phosphate builders in detergent compositions, important as they have been to the development of synthetic detergents, are known to contribute in part to eutrophication and it is most desirable to reduce the amount required to a minimum or even to entirely eliminate them as components of household detergents.

EXPERIMENTAL PROCEDURES

Two different kinds of standard soiled cotton were washed in a Terg-O-Tometer, 10 swatches per liter, with three different detergents, built and unbuilt, at different temperatures and different degrees of water hardness. Most of the experiments were with 0.25% built solutions (0.05% active ingredient plus 0.20% builder), 10 swatches per liter, 20 min at 60 C and 110 cycles per minute. Foam height was measured by the Ross-Miles test (8). Results are shown in Table I.

As in previous formulation studies (5,6) the HTAS and the NaMeαST were composites, respectively, of 6% sodium tetradecyl, 28% hexadecyl and 66% octadecyl sulfates, and of like amounts of sodium methyl α-sulfomyristate, palmitate and stearate, representing a manufactured product from hydrogenated tallow. The LAS was the isolated active ingredient from Ultrawet K (Arco Chemical Co.). The NTA was a sample from the Hampshire Chemical Division of W.R. Grace and Co. Cloths 1, and 2 were manufactured by Testfabrics, Inc. and U.S. Testing Co. Cloth 1 is more hydrophilic in composition due to the presence of aromatics, cellulosics and emulsifiers. Cloth 2 is more hydrophobic, being soiled with carbon, high molecular weight hydrocarbons and fatty oils. The washing characteristics of these cloths have been described by Ginn and coworkers (9). Sodium citrate and the inorganic salts were reagent grade.

Detergency data at different concentrations, temperatures and water hardness are shown in Table II. By analysis of variance (10) differences in ΔR of the values listed in Table I and II were significant with 95% probability.

Finally a survey of lower molecular weight sodium salts of hydroxycarboxylic acids, amino acids, dicarboxylic acids and related compounds was conducted, using the best laboratory grade chemicals available. Detergency data with HTAS, NaMeαST and LAS are listed in Table III.

DISCUSSION

In the experiments of Table I, using cloth 1, detergency was in the following order: HTAS > LAS > NaMeαST and B > Na_2SiO_3 > Na_2SO_4 (No. 1,3,5,9,10). When the active ingredient was either HTAS (No. 2) or LAS (No. 6) or a mixture of the two (No. 8) the phosphate builder can be halved without loss in detergency. Replacement of phosphate builder with Na_2SiO_3 or Na_2SO_4 resulted in a marked decrease in detergency and foaming ability (No. 9 and 10). The amount of Na_2SO_4 in the phosphate builder

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TABLE I

Foam Height and Detergency of Built Solutions in Hard Water of 300 ppm at 60 C

Solution	Weight[a] ratio, P_2O_5/A I	Detergency, ΔR^b Cloth 1	Cloth 2	Foam[c] height, mm
1. .05 HTAS[e] + .2 B[d]	1.5	45.0	15.9	185
2. .05 HTAS + .1 B	0.75	46.7	16.8	175
3. .05 NaMeαST + .2 B	1.5	28.5	13.1	215
4. .05 NaMeαST + .1 B	0.75	26.8	11.4	220
5. .05 LAS + .2 B	1.5	30.9	15.1	220
6. .05 LAS + .1 B	0.75	31.0	13.1	225
7. .025 HTAS + .025 NaMeαST + .1 B	0.75	42.9	14.6	210
8. .025 HTAS + .025 LAS + .1 B	0.75	48.0	12.2	225
9. .05 HTAS + .2 Na_2SiO_3	---	33.3	10.5	40
10. .05 HTAS + .2 Na_2SO_4	---	18.2	7.4	30
11. .05 HTAS + .1 B + .1 Na_2SO_4	0.75	46.2	17.7	160
12. .025 HTAS + .025 NaMeαST + .1 B + . Na_2SO_4	0.75	48.7	15.4	210
13. .025 HTAS + .025 LAS + .1 B + .1 Na_2SO_4	0.75	45.0	15.5	220
14. .05 HTAS + .1 NTA	---	46.8	17.3	185
15. .025 HTAS + .025 NaMeαST + .1 NTA + .1 Na_2SO_4	---	48.5	13.1	200
16. .025 HTAS + .025 NaMeαST + .1 Na Citrate + .1 Na_2SO_4	---	46.8	11.5	190
17. .025 HTAS + .025 LAS + .1 NTA + .1 Na_2SO_4	---	41.1	15.7	225
18. .025 HTAS + .025 LAS + .1 Na Citrate + .1 Na_2SO_4	---	38.8	14.3	230
19. .025 NaMeαST + .025 LAS + .1 NTA + .1 Na_2SO_4	---	24.2	12.5	210

[a]$Na_5P_3O_{10}$ and $Na_4P_2O_7$, calculated as P_2O_5 and divided by the active ingredient.

[b]Increase in reflectance after washing standard soiled cotton in a Terg-O-Tometer, 10 swatches/liter, 20 min, 110 cycles/min. Significance levels for 95% probability: 1, 1.4; 2, 0.7.

[c]Ross-Miles test (8).

[d]Phosphate builder "B" 55% of $Na_5P_3O_{10}$, 24% Na_2SO_4, 10% $Na_4P_2O_7$, 10% NaMetasilicate, 1% carboxymethylcellulose.

[e]Abbreviations: HTAS, sodium hydrogenated tallow alcohol sulfate; NaMeαST, sodium methyl α-sulfotallowate; LAS, linear alkylbenzene sulfonate; NTA, trisodium nitrilotriacetate.

formulations can be increased without loss in surfactant properties (No. 11, 12, 13). The phosphate builder can be replaced by NTA (No. 14) or sodium citrate (Table III) (No. 13) where HTAS is active ingredient or when mixed with NaMeαST (No. 15 and 16). Replacement with organic builder in HTAS-LAS mixtures caused some loss in detergency (No. 17 and 18). Under conditions of (No. 1) with cloth 1, NTA, ethylenediamine tetraacetic acid, Na_4 salt (EDTA) and sodium citrate gave ΔR values of 44.8, 44.8 and 41.7 respectively. Detergent and foaming properties of formulations containing EDTA were similar to those containing NTA and only the latter are reported in detail. A recent publication has shown some of the advantages of NTA in detergent formulations (11). With the exception of (No. 9 and 10), in all formulations involving HTAS, detergency remained at a relatively high level (38.8-48.5). Both NaMeαST and LAS, having higher foaming ability than HTAS, contribute to better foaming properties in binary mixtures containing HTAS.

Similarly for cloth 2 detergency was in the order HTAS > LAS > NaMeαST and B > Na_2SiO_3 > Na_2SO_4 (No. 1, 3, 5, 9, 10). Detergency with HTAS increased somewhat with phosphate reduction (No. 1, 2, 11). A decrease in detergency was observed for NaMeαST and LAS when the amount of phosphate builder was reduced (No. 4 and 6). HTAS produced high ΔR values with organic sequestrants: NTA (No. 14), 17.3; EDTA, 16.8; sodium citrate, 14.9. With the exception of mixtures of HTAS and LAS (No. 17), mixtures of active ingredients containing NTA as builder resulted in a slight reduction in detergency (No. 15, 16, 18, 19).

Packaged detergents with an average phosphate content, as P_2O_5, of 27% apparently contain more phosphate than would be required merely to act as a water softener in detergency. If $Na_5P_3O_{10}$ and $Na_4P_2O_7$ act to overcome water hardness at a ratio of 2 g atoms of Ca^{++} (or Mg^{++}) per mole of either phosphate, a concentration of only 0.08% B would suffice for water of 300 ppm. The ΔR values for 0.05 HTAS + 0.05B and 0.5 HTAS + 0.1B (Table I, No. 6, Cloth 1) were 29.7 and 46.7, respectively, suggesting an equivalence point for optimum detergency between 0.05 and 0.10B in agreement with the value of

TABLE II

Detergency of Built Solutions at Different Concentrations, Temperatures and Water Hardness

No.	Solution	Ratio P_2O_5/A I	Total concn., %	Temp., C	Water hardness, ppm	Detergency, ΔR^a Cloth 1	Cloth 2
1[b]	.05 HTAS	---	.05	60	0	51.1	14.4
2[b]	.05 NaMeαST	---	.05	60	0	26.4	9.0
3[b]	.05 LAS	---	.05	60	0	26.6	7.9
4	.05 HTAS + .05 B	0.38	.10	60	100	47.2	18.1
5	.05 HTAS + .1 B	0.75	.15	49	100	48.5	17.5
6	.05 NaMeαST + .1 B	0.75	.15	49	100	30.3	13.7
7	.05 LAS + .1 B	0.75	.15	49	100	30.8	14.6
8	.1 HTAS + .05 B	0.19	.15	60	300	44.5	15.4

[a]Significance levels, 95% probability 1, 1.4; 2, 0.7.

[b]Experiments without builder in distilled water.

TABLE III

Detergency of Potential Phosphate Replacements[a]

No.	0.20% Sodium Salt +	0.05% HTAS, ΔR	0.05% NaMeαST, ΔR	0.05% LAS, ΔR
1.	Glycolic acid	16.1	---	---
2.	Lactic acid	19.9	18.7	19.4
3.	Tartaric acid	23.1	19.6	20.7
4.	Gluconic acid	15.3	19.3	20.5
5.	Glycine	14.1	17.8	21.3
6.	Aspartic acid	18.9	18.2	22.5
7.	Oxalic acid	35.4	34.2	32.5
8.	Malonic acid	27.5	23.6	24.1
9.	Succinic acid	24.3	---	---
10.	Sulfoacetic	21.0	---	---
11.	Diglycolic acid	39.1	30.9	32.2
12.	Iminodiacetic acid	36.8	30.4	29.8
13.	Citric acid	43.5	30.8	34.1
14.	Phosphate builder[b]	45.0	28.5	30.9

[a]Washing conditions: 300 ppm water, 60 C, Cloth 1.
[b]Phosphate builder see Table I.

0.08%.

The pH in the experiments of Table I was in the range of 8.5-10.0 for all except the highly alkaline sodium metasilicate with a pH of 11.0. Sodium metasilicate does not function, like the phosphates, to soften water, but supplies alkalinity to assist in washing, and acts also as a corrosion inhibitor. Sodium sulfate does not usually have any important function except to add to the total weight.

In Table II the three detergents were compared again, at lower concentration, lower temperature, and in softer water. As in the experiments of Table I, HTAS was found to be the best detergent with Cloths 1 and 2. At reduced phosphate content and in only moderately hard water of 100 ppm, HTAS > LAS > NaMeαST.

A number of sodium salts of hydroxycarboyxlic acids, amino acids, dicarboxylic acids and related compounds were explored in an attempt to find new builders. The experiments, listed on Table III, were under the conditions of Table I, washed in 0.25% built solutions in hard water of 300 ppm.

Salts of glycolic, lactic, tartaric and gluconic acid gave clear solutions in hard water but low ΔR values of 13.1-23.1 for HTAS, 18.7-19.6 for NaMeαST, and 19.4-20.5 for LAS (No. 1, 2, 3, 4). The amino acids, glycine and aspartic, also formed clear solutions but were low in detergency (No. 5, 6). The salts of dicarboxylic acids, oxalic, malonic and succinic, formed preciptates in hard water and ΔR values decreased with increasing molecular weight (No. 7, 8, 9). The sodium salt of sulfoacetic acid also formed a precipitate and had a low ΔR value (No. 10).

Only two compounds were very effective. These were disodium diglycolate $O<(CH_2CO_2Na)_2$ (No. 11) and disodium iminodiacetate $HN(CH_2CO_2Na)_2$ (No. 12) which formed clear solutions in 300 ppm hard water and yielded high ΔR values for HTAS, NaMeαST and LAS.

Detergency measurements with different kinds of standard soiled cotton may be somewhat contradictory and inconclusive. Each type of cloth represents a different soil removal problem and may rank a group of detergents or detergent formulations in a slightly different order of effectiveness (9). The detergency measurements here suggest that tallow alcohol sulfates along with α-sulfo esters or linear alkylbenzenesulfonates may be a useful mixture of active ingredients on which to base detergent formulations containing little or no phosphate builder, which do not contribute to eutrophication. Tests more directly related to practical laundering such as one based on a synthetic sebum soil (12) or on household washing experiments may be necessary.

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