

Soap-based Detergent Formulations: XXVI. Hard Water Detergency of Soap-lime Soap Dispersant Combinations with Builders and Inorganic Salts¹

W.R. NOBLE and W.M. LINFIELD, Eastern Regional Research Center², Philadelphia, PA 19118

ABSTRACT

Blends of soap and 3 lime soap dispersants—the sulfated tallow alkanolamide (TAM), the coconut-oil-derived amido sulfobetaine (CAHSB) and the cocoamido betaine (CAB)—were formulated with 3 builders—sodium tripolyphosphate (STPP), trisodium nitrilotriacetate (NTA) and trisodium 2-oxa-1,1,3-propane tricarboxylate (OPT). Varying amounts of sodium sulfate were added to these formulations, and the effects of builders and sodium sulfate on detergency at 300 ppm water hardness were studied. At levels below 60%, STPP was not an effective builder for TAM formulations. Dilution of STPP-built TAM formulations with sodium sulfate substantially decreased detergency. Detergency of TAM formulations was improved by incorporation of NTA or OPT and such formulations could tolerate dilution with sodium sulfate without serious loss in detergency. NTA or STPP improved the detergency of CAB formulations but OPT did not. Addition of sodium sulfate caused some loss in detergency in all CAB formulations. Addition of STPP to CAHSB formulations caused a slight loss in detergency, but addition of NTA or OPT had no appreciable effect. Dilution of STPP-built CAHSB formulations with sodium sulfate affected detergency adversely, although not as severely as in STPP-built TAM formulations. Dilution of NTA- or OPT-built CAHSB formulations with sodium sulfate had little effect on detergency. CAB and particularly CAHSB are superior to TAM in dispersing lime soap curd. Therefore, addition of NTA, STPP, or OPT to the amphoteric formulations did not affect detergency to the same extent as in TAM formulations. Further evidence of the superiority of amphoteric lime soap dispersing agents (lsda) in dispersing lime soap curd was provided by the effectiveness of soap, CAHSB, silicate formulations in detergency studies at 1,000 ppm water hardness.

INTRODUCTION

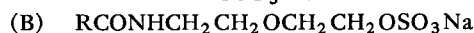
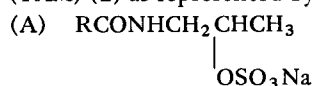
The utility of anionic and amphoteric lime soap dispersing agents (lsda) in soap-based detergents has been established (1-4). The present study covers the effects of various detergent builders on the hard water detergency of soap-lsda formulations of a wide composition range. The builders chosen for study were those that either efficiently sequester hardness ions or reduce hardness ion concentrations by an ion exchange mechanism. They were: sodium tripolyphosphate (STPP) (5), trisodium 2-oxa-1,1,3-propanetricarboxylate [OPT, NaO₂CCH₂OCH(CO₂Na)₂] (6), trisodium nitrilotriacetate (NTA) (7) and a synthetic sodium zeolite (8). STPP has been the standard builder of the detergent industry until very recently and is the most widely used of the condensed phosphates that have contributed much to the effectiveness of synthetic detergents. It has been suggested that condensed phosphates may have contributed to eutrophication, and a phosphate substitute was therefore desirable (9). In response to this environmental problem, various nonphosphate builders have been proposed either as

an adjunct to phosphate builders in formulations with reduced phosphorus content or as the sole builder in formulations intended for use in areas where phosphorus-containing detergents have been prohibited. NTA, long known as an effective sequestering agent and recommended as a laundry soap builder as early as 1938 (7), was one of the first organic builders proposed as a phosphate replacement. However, so far, its use in commercial detergents has been limited to Sweden and Canada. More recently, the experimental builder OPT (6) and the synthetic sodium zeolites (8), currently used in some commercial detergents, have been developed as complete or partial replacements for phosphates. While all of these replacement builders appear to perform adequately in detergent formulations, to date none of them has entirely replaced STPP as a detergent builder.

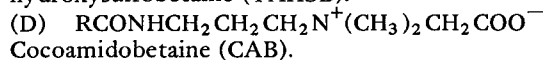
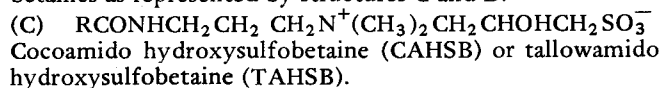
Another aspect of the present study was to examine the effect of sodium sulfate in soap-lsda detergents. Incorporation of sodium sulfate is desirable not only as a processing aid, but also as a means to reduce the cost of detergents.

Formulations containing these builders were screened for detergency at 120 F in 300 ppm hard water (as CaCO₃). A few selected formulations were also evaluated for detergency under the more stringent hardness condition of 1,000 ppm hard water, prevalent in Northern Europe, parts of Canada and elsewhere.

The anionic lsda and the amphoteric lsda used in this study were selected for their superior performance in soap-lsda detergents from among those previously studied in this laboratory. The anionic lsda was the sulfated mixture of isopropanolamides and diglycolamides of tallow fatty acids (TAM) (2) as represented by structures A and B.



The amphoterics were either amidosulfobetaines or amido-betaines as represented by structures C and D.



Because the coco derivative of structure C is commercially available, it was studied more extensively.

EXPERIMENTAL PROCEDURES

Materials

The soap used in the study was Bradford Supreme Rice (Original Bradford Soap Works, Inc., West Warwick, RI). An experimental lot of TAM was supplied by Henkel, Inc., Hoboken, NJ. CAHSB (Varion CAS) was obtained from

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²Agricultural Research, Science and Education Administration, U.S. Department of Agriculture.

Ashland Chemical Co., Columbus, OH, and CAB (Lexaine C) from Inolex Corp., Philadelphia, PA. Tallow sulfobetaine (TSB), tallowamido sulfobetaine (TASB) and TAHSB were prepared in the laboratory (3,4). Sodium metasilicate pentahydrate (Metso) was obtained from Philadelphia Quartz Co., King of Prussia, PA, OPT (an experimental lot of Builder M) from the Monsanto Co., St. Louis, MO, NTA from Aldrich Chemical Co., Inc., Milwaukee, WI, the synthetic sodium zeolite (Sasil) from Henkel KGaA, Düsseldorf, Federal Republic of Germany and CMC (7LT) from Hercules, Inc., Wilmington, DE. STPP was a standard laboratory reagent.

Test Methods

In calculating the amount of lsdA to be used in a test formulation, it was necessary to take into consideration that the lsdA samples were usually impure and therefore only partly surface active. The percentage of active matter of the TAM samples was determined by a two-phase titration with 0.001 N Hyamine 1622 (Rohm and Haas Co., Philadelphia, PA) solution and 2,7-dichlorofluorescein indicator (10). The percentage of active matter of amphoteric samples was determined by the HPLC method of Parris et al. (11). In all of the formulations listed in this paper, the percentages of lsdA refer to the active matter as determined analytically.

Detergency determinations were conducted with a Tergotometer (U.S. Testing Co., Inc., Hoboken, NJ). Three commercial soil cloths were used in the washing tests: Test-fabrics (TF) polyester-cotton (65/35) cloth with a permanent press finish, EMPA 101 (E-101) cotton cloth and EMPA 104 (E-104) polyester-cotton (65/35) cloth with a permanent press finish. Fifteen 4-in. diameter swatches, 5 of each cloth type, were washed together with 2 g of a detergent formulation dissolved in 1 l hard water (as CaCO_3) for 20 min at 110 cycles per min. The wash temperature was 120 F when washing was in 300 ppm hard water and 190 F in 1,000 ppm hard water. Detergency was measured as the increase in reflectance (ΔR) after washing. Reflectances were determined with a Neotec Tru-Color colorimeter (Neotec Corp., Silver Spring, MD 10910). The ΔR

values were averages of 10 readings—2 for each swatch. Two commercial United States household detergents were used as controls in the experiments conducted at 120 F and 300 ppm hardness. One control was a low phosphorus detergent (3% P), and the other a high phosphorus detergent (12% P). The detergency data shown in Figures 1-6 are expressed as a percentage of the detergency of the 3% P control. A difference of less than 8% between any 2 detergency values was not statistically significant. Table I relates the performance of 3% P control to that of the 12% P. In addition, a commercial German household detergent, formulated for use at high temperature and high hardness, was used as the control for the washing experiments at 190 F and 1,000 ppm.

RESULTS AND DISCUSSION

The washing performance of household-type detergents consisting of tallow soap, an lsdA and a sodium silicate has been reported in earlier publications (1-4) of this series. Table II briefly summarizes the washing performance of 3 examples of this type of formulation for the lsdA TAM, CAB and CAHSB and shows the effect of sodium sulfate dilution on the formulations. In the absence of sodium sulfate, detergency was approximately the same for all 3 lsdA. However, when the TAM formulation was diluted with sodium sulfate, detergency decreased to an unacceptable level. The CAB and CAHSB formulations, on the other hand, suffered only a slight loss in detergency when diluted with sodium sulfate. It is likely that formulations based on anionic lsdA, such as TAM, are sensitive to inorganic salts due to a salting out effect of the electrolyte, whereas those based on amphoteric lsdA, such as CAB and CAHSB, which are electronically neutral, are unaffected. It is also noteworthy that the betaine CAB performs as well as the sulfobetaine CAHSB under the test conditions of 120 F and water hardness of 300 ppm (as CaCO_3).

Table III shows the general formulation scheme for the incorporation of the builders NTA, STPP and OPT into soap-lsdA-silicate blends. Formulations 1-4 were without sodium sulfate, whereas formulations 5-10 contained varying amounts of sodium sulfate. In formulations 5-7, the builder content varied from 25 to 45%; but in formulations 8-10, the builder content was held constant at 30%. Formulations 8-10 were used only for TAM blends built with NTA or OPT, and for CAB blends built with NTA. All other series of experimental blends were represented by formulations 5-7. Figures 1, 3 and 5 are plots of detergency (expressed as a percentage of the detergency of the control detergent) as a function of builder content. As the builder content increased, the soap and lsdA contents decreased proportionately. In these plots, as well as those of the sodium-sulfate-containing formulations, the soap-to-lsdA

TABLE I
Detergency of Control Detergents at 120 F and 300 ppm

	Detergency (ΔR)		
	TF	EMPA 101	EMPA 104
3% P Control	30	29	28
12% P Control	34	33	33

TABLE II

Detergency of a Soap-LSDA- Na_2SiO_3 Formulation with and without Na_2SO_4 (120 F, 300 ppm)

Composition of formulations				Detergency ^a								
				TAM formulations			CAB formulations			CAHSB formulations		
Soap %	LSDA %	Na_2SiO_3 %	Na_2SO_4 %	TF	EMPA 101	EMPA 104	TF	EMPA 101	EMPA 104	TF	EMPA 101	EMPA 104
63.8 ^b	21.2 ^b	15.0 ^b	—	104	110	121	100	107	114	103	115	121
57.4	19.1	13.5	10.0	108	86	96	100	100	103	103	107	110
51.0	17.0	12.0	20.0	79	76	67	100	93	103	103	100	107

^aCalculated as a percentage of the detergency of that of the control detergent. A difference of 8% between any 2 values is statistically significant.

^bFormulation 1 in Table III.

TABLE III

Formulations of Soap-LSDA Blends with Builders, Sodium Metasilicate and Sodium Sulfate

Formulation	Soap %	LSDA %	Builder %	Na ₂ SiO ₃ %	Na ₂ SO ₄ %
1	64	21	—	15.0	—
2	52.5	17.5	20.0	10.0	—
3	37.5	12.5	40.0	10.0	—
4	22.5	7.5	60.0	10.0	—
5	37.5	12.5	25.0	10.0	15.0
6	22.5	7.5	40.0	10.0	20.0
7	15.0	5.0	45.0	10.0	25.0
8 ^a	33.8	11.2	30.0	10.0	15.0
9 ^a	30.0	10.0	30.0	10.0	20.0
10 ^a	26.0	9.0	30.0	10.0	25.0

^aTAM-OPT, CAB-NTA and TAM-NTA formulations only.

ratio was 3/1 for all formulations. Figures 2, 4 and 6 are plots, similar to Figures 1, 3 and 5, of sodium-sulfate-containing formulations in which detergency is plotted as a function of sodium sulfate content. The sulfate-containing formulations 5-7 (Table III) derive from the nonsulfate formulations in Figures 1, 3 and 5, whereas the sulfate containing formulations 8-10, those with a constant builder content of 30%, do not. In each figure, the composition corresponding to each data point is indicated by the formulation number, shown at the top of the figure, and is given in Table III.

TAM formulations (Fig. 1)

All NTA and OPT formulations had detergency values in excess of 100% (100% designates the detergency of the control detergent). In the case of STPP, only the formulations with 0 and 60% STPP had detergency values greater than 100%. Formulations at intermediate STPP levels exhibited much poorer detergency, particularly at a 20% STPP level. When sodium sulfate was added as a diluent as shown in Figure 2, the detergency of STPP formulations dropped even more. NTA and OPT formulations exhibited only a slight loss in detergency. At low levels (20-40%), the effect of STPP on TAM formulations is not only negative, but of the same order of magnitude as that of sodium sulfate. At very high levels (60%), the effect of STPP is bene-

ficial. This extreme variation in detergency with STPP concentration is not readily explained but appears to involve some sort of interaction between the anionic lsd and STPP, since this effect has only been observed with anionic lsd.

CAB Formulations

Figure 3 shows that all CAB formulations, regardless of the choice of builder, had detergency values equal to or greater than those of the control detergent. Addition of sodium sulfate as a diluent, as shown in Figure 4, caused a loss in detergency. However, of all the data points for sulfate-containing formulations, only 2 had values of less than 100%.

CAHSB Formulations

NTA- and OPT-built formulations were all excellent in washing performance (Fig. 5), whereas STPP formulations did not perform as well as the formulations built with these 2 organic builders. Dilution with sodium sulfate (Fig. 6) further increased the disparity between STPP-built formulations and the formulations built with the 2 organic builders. The detergency of all STPP + Na₂SO₄ formulations was less than 100% for the 2 polyester-cotton cloths, TF and E-104. The NTA- and OPT-built formulations, on the other hand, lost little detergency upon dilution with sodium sulfate.

Overall, the performance of TAM and CAHSB formulations built with the 2 organic builders was superior to those built with STPP, whereas all 3 builders performed equally well in CAB formulations. The 2 amphoteric lsd were superior to the anionic TAM and were less sensitive to sulfate dilution. However, the drastic loss in detergency on sulfate dilution of TAM formulations can be avoided by formulating with either of the 2 organic builders, particularly OPT, in place of STPP.

Although not reported in detail here, the washing performance of experimental formulations in which the lsd was either of the 2 amphoteric,

RCONHCH₂CH₂CH₂N⁺(CH₃)₂CH₂CH₂CH₂SO₃⁻ (TASB), or RN⁺(CH₃)₂CH₂CH₂CH₂SO₃⁻ (TSB),

where R is tallow-derived, was nearly equivalent to those in which CAHSB or CAB were the lsd.

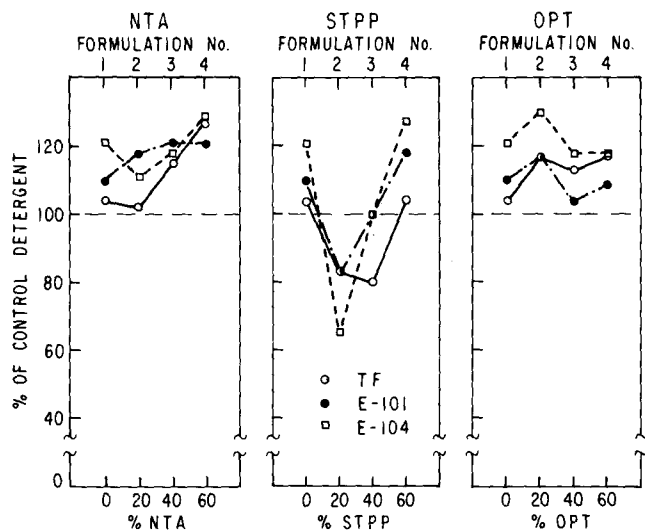


FIG. 1. Detergency of blends of soap, TAM, sodium metasilicate and varying amounts of builders at 120 F and 300 ppm water hardness.

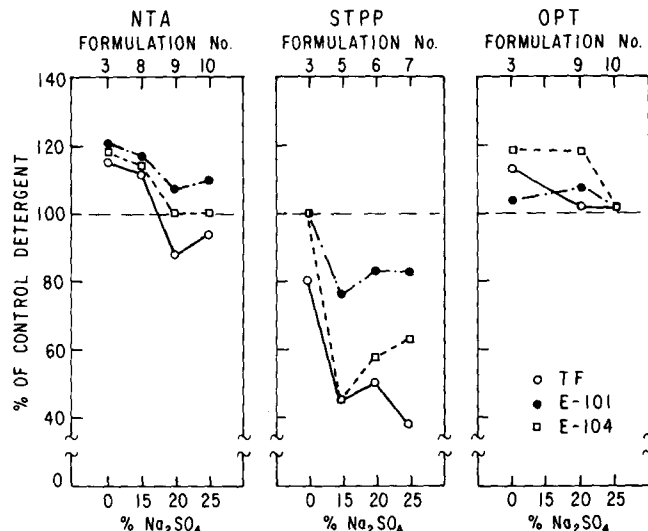


FIG. 2. Detergency of blends of soap, TAM, sodium metasilicate, builder and varying amounts of sodium sulfate at 120 F and 300 ppm water hardness.

BUILT SOAP-BASED DETERGENTS

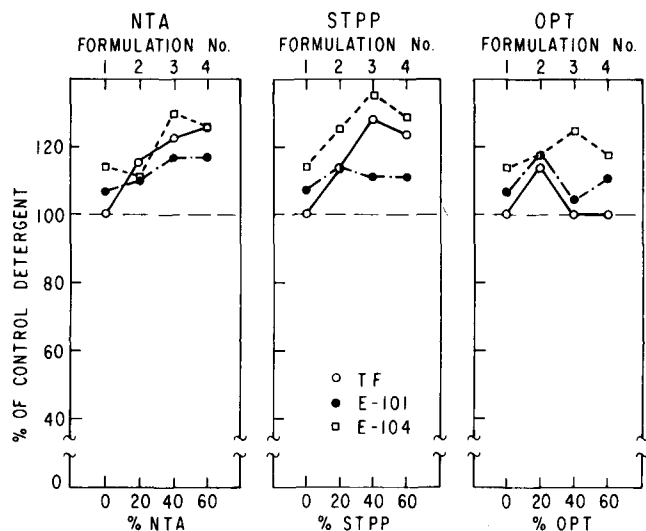


FIG. 3. Detergency of blends of soap, CAB, sodium metasilicate and varying amounts of builders at 120 F and 300 ppm water hardness.

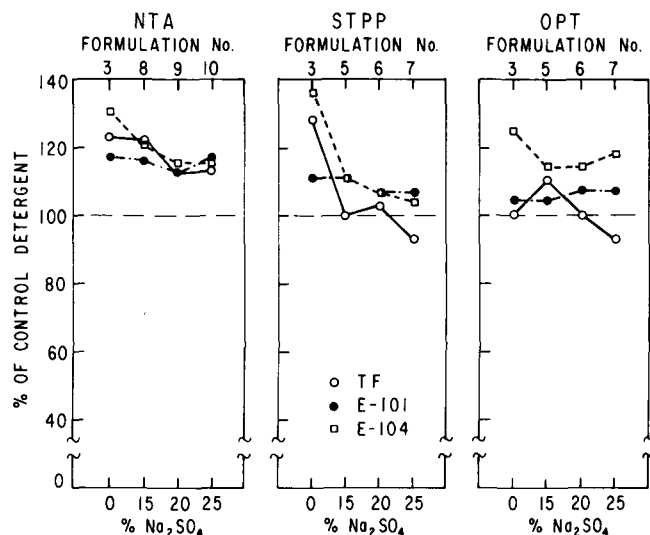


FIG. 4. Detergency of blends of soap, CAB, sodium metasilicate, builder and varying amounts of sodium sulfate at 120 F and 300 ppm water hardness.

Formulations Built with Zeolites

Although synthetic sodium zeolites are used effectively in some commercial detergents, they were not effective in improving the detergency of soap-lsda-silicate blends. For example, the best detergency values of TAM-zeolite formulations were 65% of the control value for E-101 cotton cloth and 70% of the control value for E-104 polyester-cotton cloth. Because of the generally poor results obtained with zeolites, the data are not reported here in detail.

Washing at High Temperature and High Hardness

Figure 7 shows the results of a detergency study, at 190 F and 1,000 ppm water hardness (as CaCO₃), for a blend of 64% soap, 21% CAHSB, 15% Na₂SiO₃ and for this formulation progressively diluted with 10, 20, 30, 40 and 50% sodium sulfate, respectively. The control detergent was a commercial German detergent formulated for high hardness and high laundering temperature. Although the 2 polyester-cotton cloths, TF and E-104, exhibited some loss in deter-

gency for the formulations containing 40 and 50% sodium sulfate, all detergency values far exceeded those of the control detergent. An identical experimental series in which the lsda was TAHSB, the tallow analog of CAHSB, yielded similar results. The detergency results with TAHSB were slightly poorer than those with the CAHSB formulations, but they were still much superior to the European detergent. These findings are quite surprising since the amount of hard water ions is roughly 3 times that required to tie up all soap as the calcium salt.

Similar formulations differing only in that either TAM or CAB was the lsda were tested for detergency at 190 F and high hardnesses. Washing performance of these was very poor, not only at 1,000 ppm but also at 500 ppm water hardness. This loss in detergency could not be ascribed entirely to the effect of sodium sulfate; formulations without sodium sulfate were as poor as those with it. Evidently the explanation is that TAM or CAB, which are less effective lsda than CAHSB, were unable to disperse lime soap under these high hardness washing conditions. To

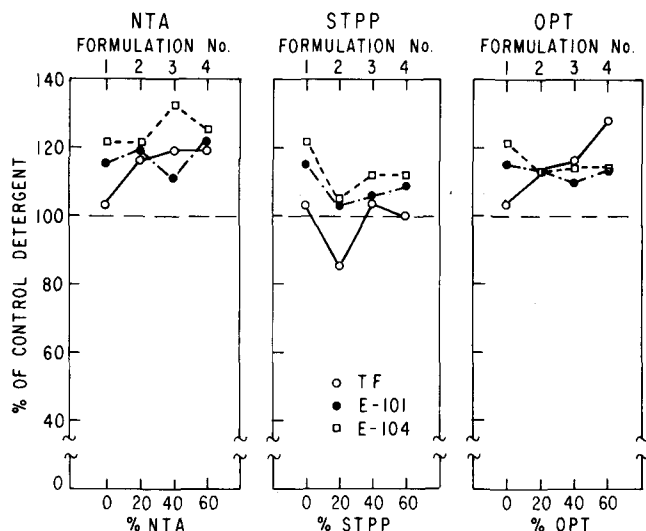


FIG. 5. Detergency of blends of soap, CAHSB, sodium metasilicate and varying amounts of builders at 120 F and 300 ppm water hardness.

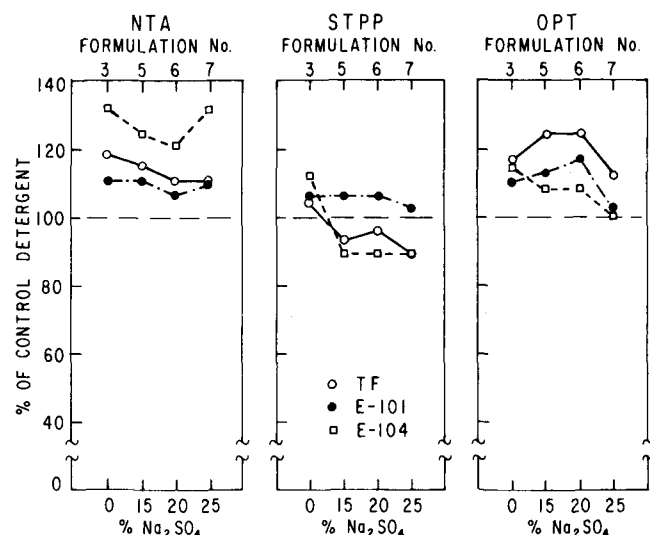


FIG. 6. Detergency of blends of soap, CAHSB, sodium metasilicate, builder and varying amounts of sodium sulfate at 120 F and 300 ppm water hardness.

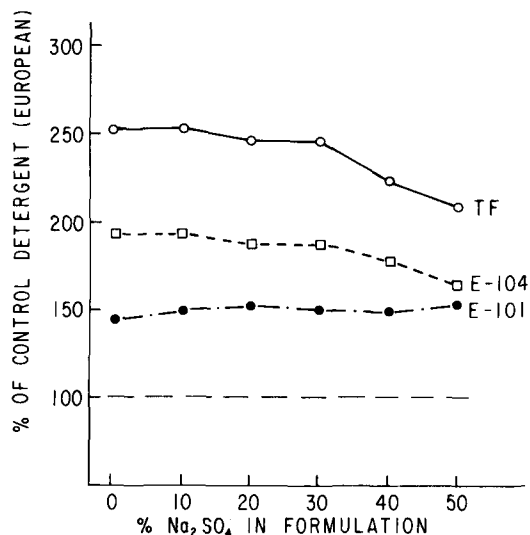


FIG. 7. Detergency of blends of soap, CAHSB, sodium metasilicate and varying amounts of sodium sulfate at 190 F and 1,000 ppm water hardness.

be effective under these conditions, the lsda should be an amphoteric with a strong cationic site, such as a quaternary ammonium group, and a strong anionic site, such as a sulfonate group. The structure of CAHSB fulfills these requirements, whereas that of CAB does not. The question of whether the loss in detergency by TAM or CAB formulations was primarily due to the increased temperature or the increased hardness was resolved by experiments carried out at 190 F and 300 ppm hardness in which TAM, the least effective of the 3 compounds in dispersing lime soap curd, was the lsda. Washing performance was acceptable,

indicating that the higher hardness was the limiting factor rather than the high water temperature. The lack of stability of CAB formulations under high hardness conditions is particularly interesting in view of the excellent washing performance and stability to strong electrolytes of CAB formulations in 300 ppm hard water. The failure of CAB to disperse lime soap curd at the higher hardness emphasizes the need for an amphoteric with both strong cationic and anionic sites.

The detergency of soap, TAM, silicate combinations can be improved by incorporation of OPT or NTA. More importantly, TAM formulations incorporating either of these 2 builders can tolerate sodium sulfate dilution without serious loss in detergency. Formulations based on CAB or particularly CAHSB were not improved to the same extent, probably because they are superior to TAM in dispersing lime soap curd. CAHSB formulations performed exceptionally well at 1,000 ppm hardness when the only builder was a silicate.

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