Synthetic High Molecular Weight Linear Alkyl[1] Sulfates in Heavy Duty Detergents

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Abstract

High molecular weight alcohol derivatives, when blended with linear alkyl sulfates (LAS), produce high performing soil removal systems which exhibit improved water solubility over that of the alkyl sulfate alone. The foam profile of the mixed active product may also be designed to yield either moderate or high foaming products. Studies of blend ratios, active concentrations and builder effects are presented to optimize performance. Blend ratios which exhibited considerable interest ranged from 1 part LAS per 2 parts high molecular weight synthetic alcohol sulfate (HMWAS) to 1.5 parts LAS per 1 part HMWAS. Evaluations were conducted on soil removal with cellulosic and synthetic fabrics and foam stability. The effects of foam boosters, water hardness and temperature are also measured as foam modifiers. Synthetic lauryl alcohol was shown to be an effective foam booster in these systems.

Introduction

Sulfated linear primary alcohols are known as effective detergents and surface active agents. The literature abounds with references to the investigation of the high molecular weight compounds (C_{16}–C_{18}) in heavy duty detergents products (1–6). Because of the somewhat limited solubility of these high molecular weight alcohol derivatives at room temperature, they are generally formulated into multifunctional surfactant active systems for household use.

A large number of patents have been issued in many areas of the world describing various commercial projects for the use of high molecular weight alcohol sulfates (HMWAS) in detergent products (7–17).

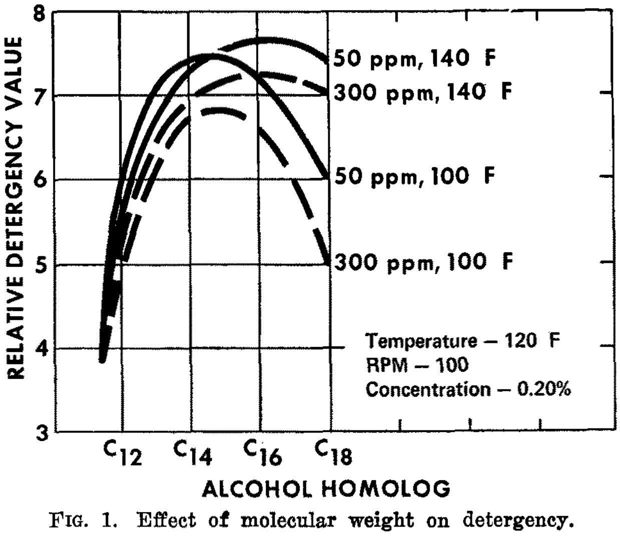

FIG. 1. Effect of molecular weight on detergency.

TABLE I
Molecular Weight Distribution of Synthetic Primary Alcohols

Compound	Mol. weight	Per cent
n-Tetradecanol	$C_{14}OH$	2.5
n-Hexadecanol	$C_{16}OH$	49.1
n-Octadecanol	$C_{18}OH$	31.6
n-Eicosanol	$C_{20}OH$	16.8

In addition to the excellent detergency properties, these products also exhibit improved biodegradability in both aerobic and anaerobic conditions (18,19). As reported by Maurer et al. (19), ". . . under anaerobic conditions of sludge digestion . . . The alcohol sulfates were found to be readily and completely degraded."

Recent work by this laboratory on the use of high molecular weight range synthetic linear primary alcohol sulfates in combination with LAS has enumerated the significant variables controlling both soil removal and foam in these mixed active systems.

Experimental Procedures

Methods

The soil removal studies were conducted in a built heavy duty formulation containing 50% sodium tripolyphosphate, 5% sodium metasilicate, 0.8% carboxymethylcellulose, and the balance sodium sulfate and water. Fluorescent whitening agents, dyes and perfumes were omitted from the formulas for this work, for the sake of simplicity. The first test series were conducted in a Terg-O-Tometer at our standard laboratory operating conditions on three different types of standard soiled cotton. (United States Test-

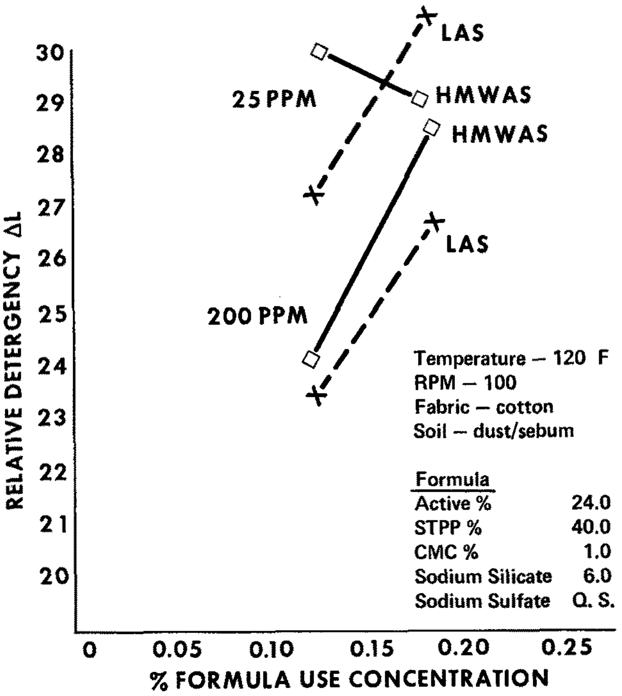

FIG. 2. Effect of water hardness and concentration on detergency.

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[1] Presented at the AOCS Meeting, New York, October, 1968.

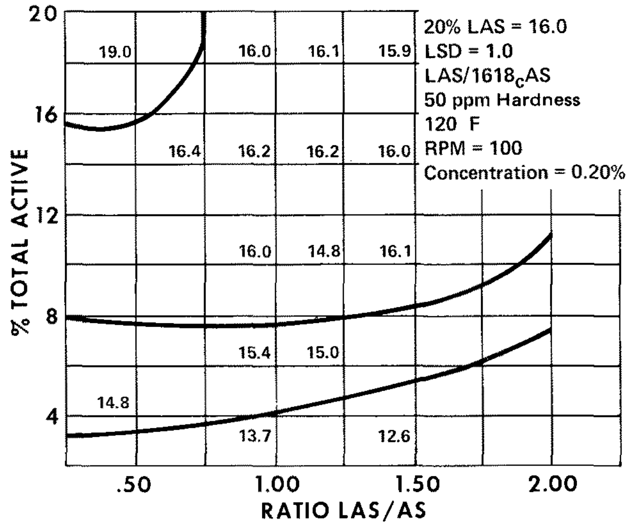

FIG. 3. Effect of ratio and concentration on detergency.

ing Labs., Test Fabrics Inc., and ACH No. 115) Three 4 × 4 in. samples of each soiled cloth were placed in a single test pot and washed simultaneously. This method provided a soil load consisting of nine soiled cloths per test. A second series of tests on cotton, polyester and polyester-cotton blend fabrics soiled at our laboratory with a dust-sebum soil (20) was also conducted in a Terg-O-Tometer at conditions of underuse and normal use levels. These tests were also run with nine soiled swatches cut into 4 × 4 in. squares.

The foam characteristics were measured by both manual dishwashing tests and a washing machine foam test.

The Terg-O-Tometer data was statistically treated to determine the least significant differences between products at a 95% confidence level. The dishwashing foam data was compared to internal performance variables to establish significant differences and the washing machine tests were evaluated by subjective observations of paired comparisons. In all cases, sufficient replications were run to establish statistical significance.

Reflectance measurements were made using a Hunter Laboratories Color Difference Meter, Model D-25, and the relative soil removal values were compared as Δ L.

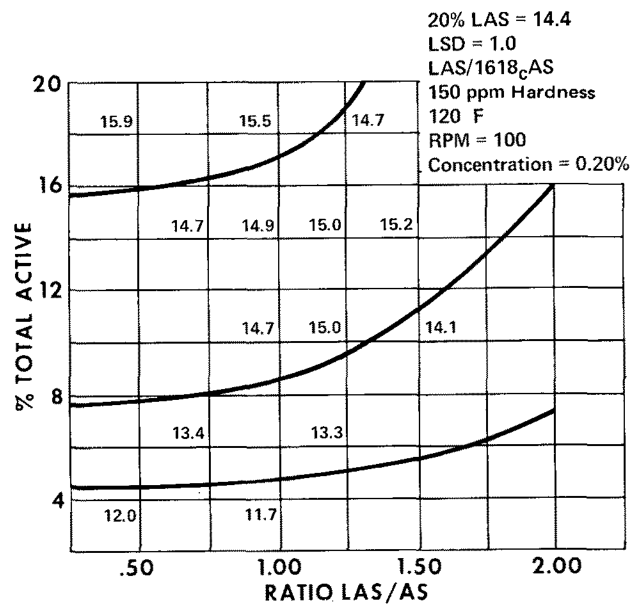

FIG. 4. Effect of ratio and concentration on detergency.

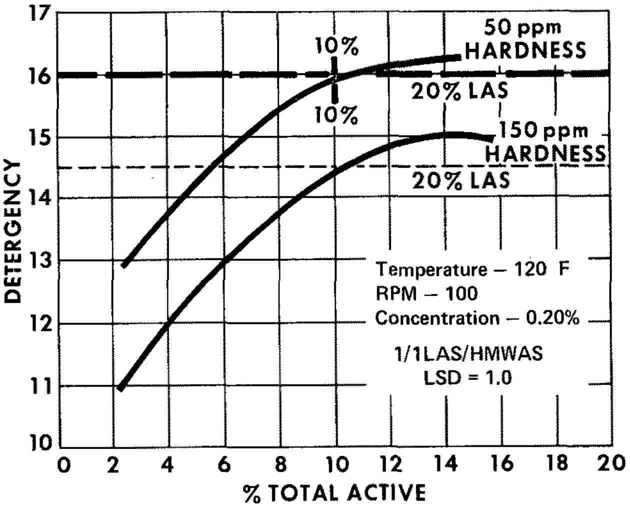

FIG. 5. Effect of concentration on detergency.

Materials

The HMWAS ($ROSO_3Na$) for this work was prepared in our laboratory by the sulfation of synthetic linear primary alcohol with chlorosulfonic acid. We have also sulfated this synthetic alcohol with both laboratory and commercial sulfur trioxide falling film reactors. The alcohol was derived from the polymerization of ethylene and contained the following typical homolog distributions (Table I).

This commercially available alcohol had an average molecular weight of 272. The LAS was a commercial variety of a high 2-phenyl linear tridecylbenzene sulfonate with an average molecular weight of 362 for the sodium sulfonate salt. The purification procedures and the surfactant products for this work were the same as would be the custom in a commercial detergent manufacturing plant.

Discussion and Results

Detergency

The Ziegler polymerization process yields a homologous series of synthetic fatty alcohols.

The option suggested by this variety of commercially available linear primary fatty alcohols demanded that we turn our attention to optimizing the molecular weight of the alcohol sulfate to be used in this work. Figure 1 shows the effect of molecular weight on detergency, at high and low temperatures. HMWAS have limited solubility at room temperature (approximately 0.7% by weight) and the data on this plot are entirely consistent with this fact. The HMWAS yield superior detergency, although this benefit may best be obtained at elevated temperature (above 120 F) to favor their solution.

The effect of concentration on detergency was found to be less significant with HMWAS as com-

TABLE II
Washing Machine Foam:
Effect of LAS-HMWAS Ratio and Total Active Product[a]

Total active, %	Ratio LAS-HMWAS, 5 and 10 Min. Readings							
	0.6:1		1:1		1.2:1		1.4:1	
	5	10	5	10	5	10	5	10
10	¼	¼	¼	¼	½	½	½	½
14	1	1	1	1	1¼	1¼	1½	1½
18	1¼	1½	1½	1½	1½	1¾	1¾	2

[a] Hardness, 90 ppm; temperature, 130 F; water, 3.5 oz avdp/16 gal; soil load 1.0 oz/16 gal water.

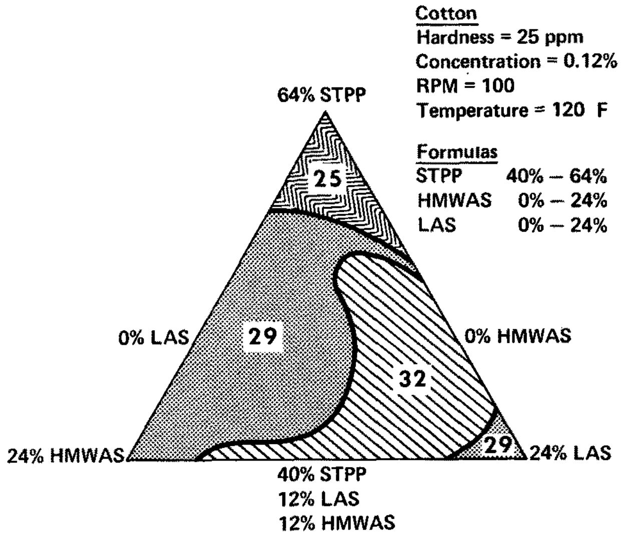

FIG. 6. Relative detergency in heavy duty laundry formulations.

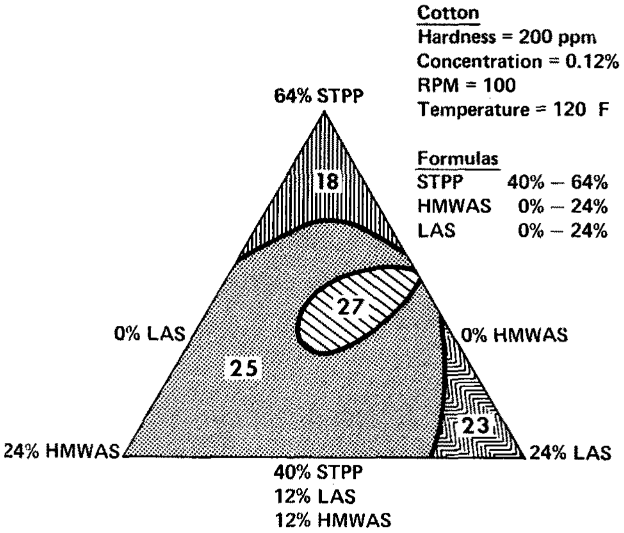

FIG. 7. Relative detergency in heavy duty laundry formulations.

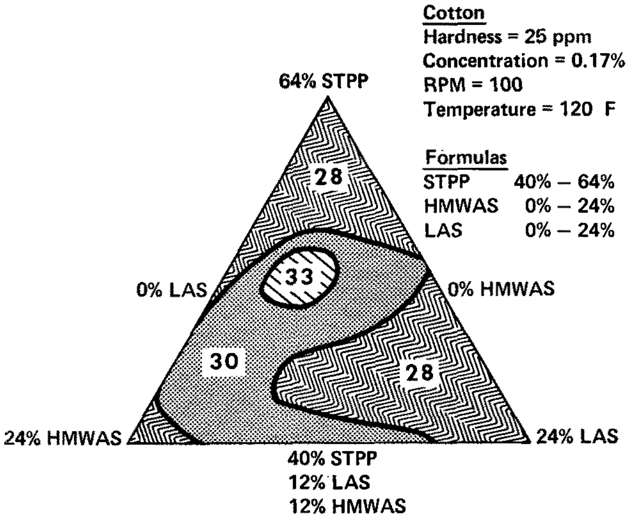

FIG. 8. Relative detergency in heavy duty laundry formulations.

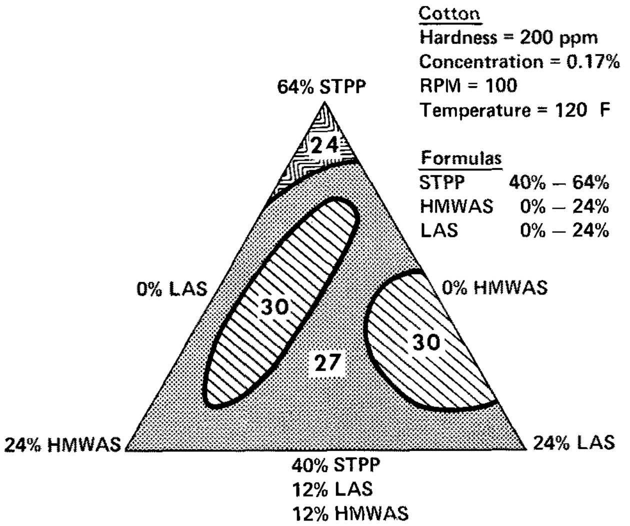

FIG. 9. Relative detergency in heavy duty laundry formulations.

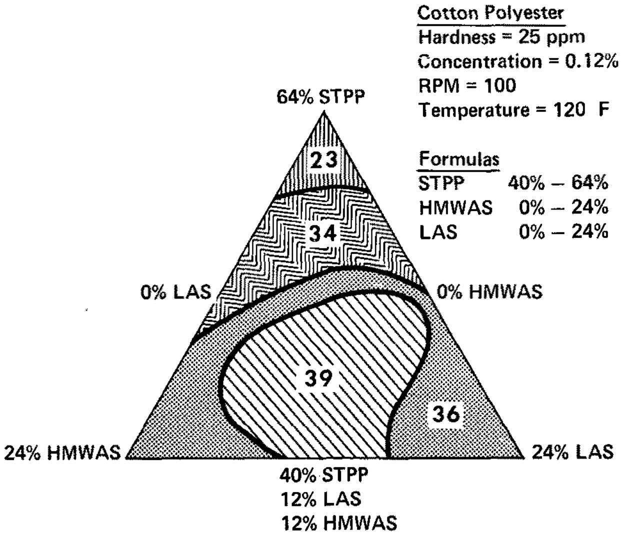

FIG. 10. Relative detergency in heavy duty laundry formulations.

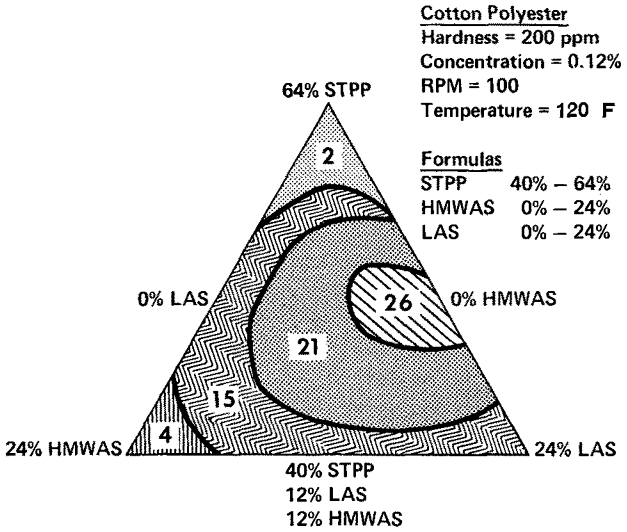

FIG. 11. Relative detergency in heavy duty laundry formulations.

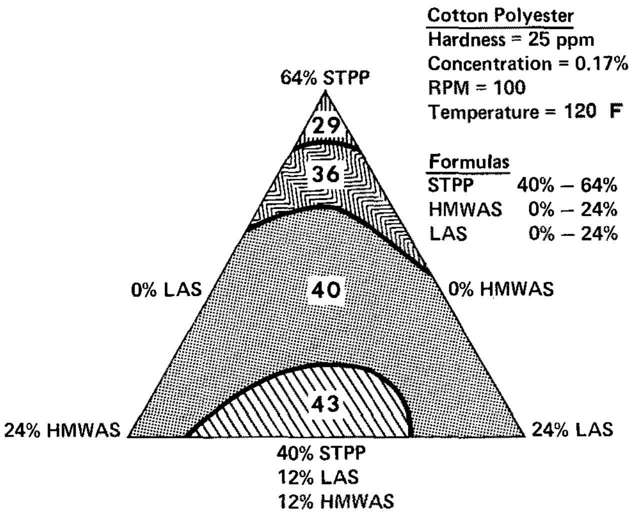

FIG. 12. Relative detergency in heavy duty laundry formulations.

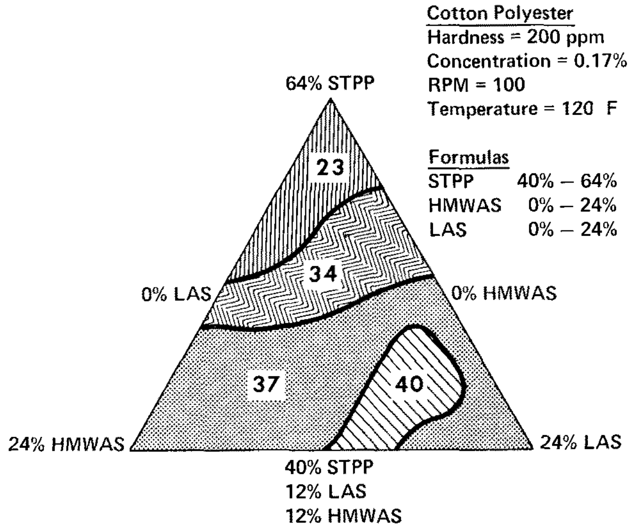

FIG. 13. Relative detergency in heavy duty laundry formulations.

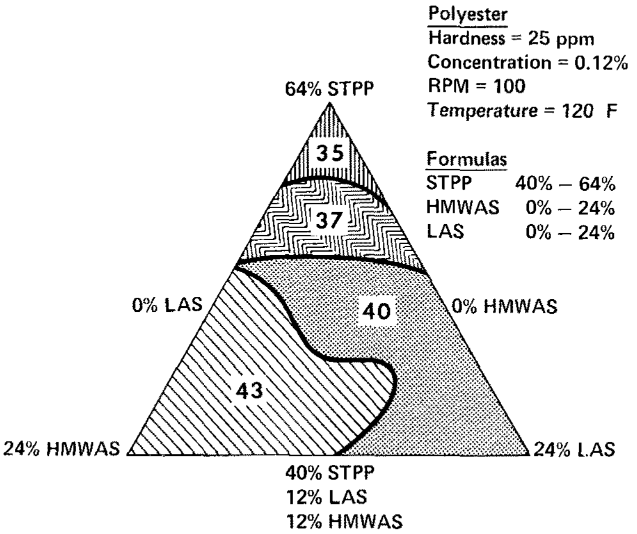

FIG. 14. Relative detergency in heavy duty laundry formulations.

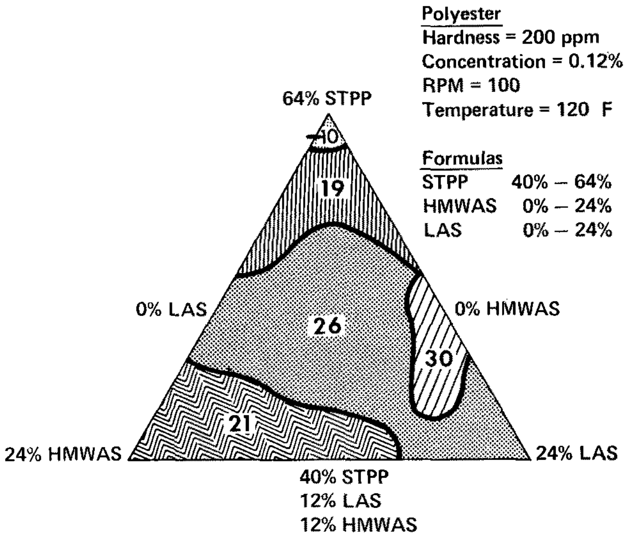

FIG. 15. Relative detergency in heavy duty laundry formulations.

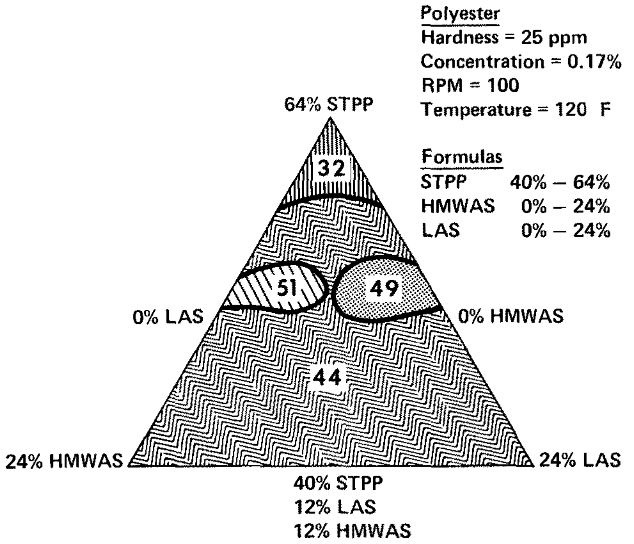

FIG. 16. Relative detergency in heavy duty laundry formulations.

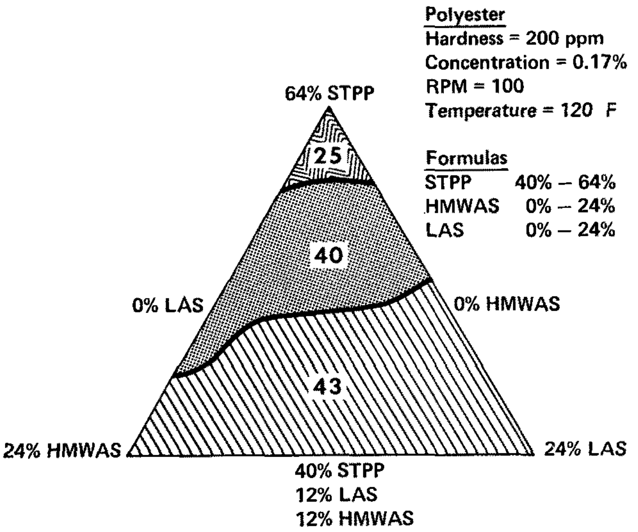

FIG. 17. Relative detergency in heavy duty laundry formulations.

TABLE III
Washing Machine Foam:[a] Effect of Hardness

Hardness	C_{16}-65%, C_{18}-35% AS	
	5 min	10 min
50	1½	1¾
90	1½	1
300	0	0

[a] Temperature, 130 F; water, 3.5 oz avdp/16 gal; LAS-AS ratio, 1.0:1.5; total active, 12%; soil load, 1.0 oz/16 gal water.

pared to LAS. This was especially true in soft water. Figure 2 shows these effects at two use levels, 0.12% and 0.17%, chosen by our laboratory to represent typical household under use and normal use levels. With this preliminary work completed, our attention was drawn to the mixed active systems composed of HMWAS and LAS. Optimization studies of these systems showed the desirable effects of blending these surfactants and a synergism between HMWAS and LAS was noticed. Figure 3 shows the effect of blend ratio and total active concentration on detergency at 50 ppm water hardness. The very apparent preferential area in the upper left hand corner representing the higher HMWAS content blend ratios and higher total active levels were not surprising to find, and are, in fact, entirely consistent with our previous findings. A very significant observation is also quite evident and that is the secondary performance level area (that which is equal to 20% LAS alone). One may vary the HMWAS-LAS ratio from 0.50 to 1.50 and the total active weight per cent from 10 to 20, without affecting a significant increase or reduction of the performance level of the formula. This fact then can be useful in designing a heavy duty household laundry product to achieve other goals which may be favored by a preponderance of either component of the system. Figure 4 contains similar data as Figure 3, but at 150 ppm water hardness. Again, the optimum performance area favors higher HMWAS levels in the blend and the secondary performance region (equal to 20% LAS) allows for a broad ratio range in the formula. Very often we may be concerned with the economics of a proposed new formulation; Figure 5 presents the data somewhat differently to show the points of equivalent performance between a 1:1 mixed HMWAS-LAS formula and 20% LAS. We note that this equivalency occurs at about one half of the active content of the LAS for the blended product.

Current testing programs, to be of general interest, must include work on a variety of fabrics and soils. Three cloths obtained from commercial mills (cotton, cotton-polyester 65:35 blend, and polyester) were soiled in our laboratory with a dust-sebum mixture (20). A series of soil removal and whiteness retention tests were run at varying ratios of HMWAS and LAS in a number of heavy duty test formulations. The sodium tripolyphosphate was varied from 40% to 64% and the surfactant active content ranged from 0% to 24% and was complimentarily modified to total a sum of 64% for the phosphate-surfactant combination. These tests were run at two water hardness levels (25 ppm and 200 ppm) and at two use concentration (0.12% and 0.17%). A family of trifunctional charts was prepared to demonstrate the formula areas of optimum performance for each fabric at each test condition. The indicated relative detergency performance values are comparative within each fabric, and should not be compared between cloths. Figure 6 contains this data for cotton at 25 ppm water hardness and 0.12% use concentration.

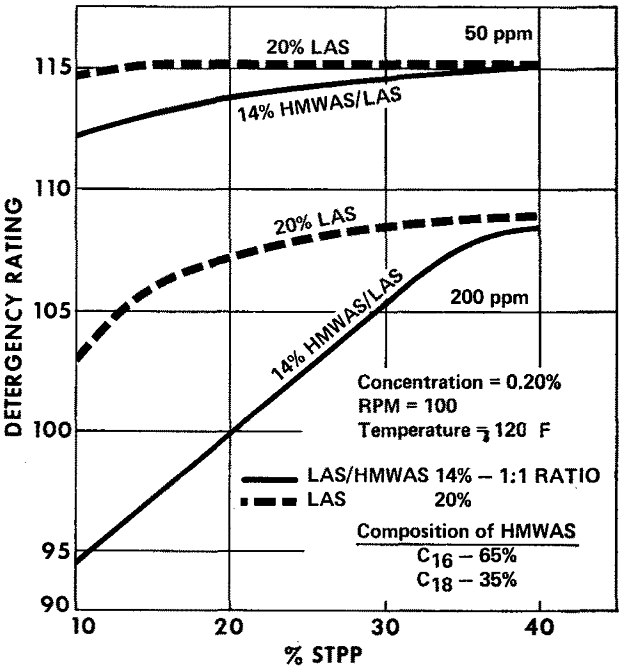

FIG. 18. Effect of phosphate on detergency.

The primary performance area is shown as a swath across the chart and implies that at lower phosphate levels the best performance tends towards higher HMWAS content. With an increase in water hardness to 200 ppm (Fig. 7) the optimum region is shifted towards higher tripolyphosphate formulas. This important high phosphate content requirement for optimum HMWAS performance is a theme which we will see repeated throughout this discussion. At higher, more normal use concentration, in soft water (Fig. 8) the optimum performance area is more concentrated and represents a higher performance level. The benefit of HMWAS is in evidence, although the total experiment variation is relatively slight at this condition. Hard water testing showed two equivalent high performance areas for HMWAS-LAS blends (Fig. 9).

Synthetic fabrics constitute an increasing percentage of the wash load, and cotton-polyester blends are of particular importance at this time. The next eight graphs show that there are much greater differences between the performance plateaus on poly-

TABLE IV
Washing Machine Foam:[a] Effect of Total Active and Foam Booster

Product	Foam booster	12% Active		16% Active		5 min	10 min
		5 min	10 min	5 min	10 min		
C_{16}-65%; C_{18}-35%	None	1½	1	1½	1½		
C_{16}-65%; C_{18}-35%	2%, COCO MEA + 2 Mols Ethylene Oxide	1½	1½	......	......		
C_{16}-65%; C_{18}-35%	2%, Linear primary alcohol	1¾	1¾	1¾	1¾		
C_{16}-65%; C_{18}-35%	2%, Linear primary alcohol	1¾	1½	......	......		
Commercial medium foamer A						½	¾
Commercial high foamer B						1¼	1½

[a] Hardness, 90 ppm; temperature, 130 F; concentration, 0.36%; LAS-HMWAS ratio 1.0:1.5; soil load, 1.0 oz/16 gal water.

TABLE V
C_{16}-65%, C_{18}-35% AS
Dishwashing Foam Stability: Effect of Foam Boosters[a]

Products	Plates washed	
	50 ppm	300 ppm
Commercial medium foamer A	18	24
Commercial high foamer B	18	33
12% Total Active, 1.0–1.5 LAS per C_{16}-65%, C_{18}-35%	16	3
2% LIPA	22	12
2% Linear primary alcohol	24	10
2% Ethoxylated amide	20	12
1% Ethoxylated amide + 1% linear primary alcohol	25	10
4% LIPA	26	24
2% LIPA + 2% linear primary alcohol	23	21
2% Ethoxylated amide + 2% linear primary alcohol	25	19

[a] Temperature, 115 F; concentration, 0.125%.

ester and polyester blends than were evident with cotton alone. The optimum regions are more clearly defined, and the response is more sensitive to smaller formula changes. Figure 10 illustrates the relative performance on cotton-polyester at 25 ppm water hardness and 0.12% concentration, a definite under use level for cleaning synthetic fabrics. Clearly, the best systems favor higher surfactant concentrations of the mixed HMWAS-LAS product. Figure 11 reiterates the phosphate dependency that is demanded for the best high molecular weight alkyl sulfate performance. When the detergent concentration is increased, as seen in Figure 12, the mixed active system is clearly shown to be best as compared to the other products. It is clear, also, that the high ratio of surfactant to phosphate is favored. This is consistent in soft or hard water. Figure 13 shows the same relationship for 200 ppm water hardness. It is important to observe that formulas containing very high tripolyphosphate content and, conversely, low surfactant levels are exceptionally poor at under use levels for the synthetic fabric blend as compared to cotton. This fact then again confirms the necessity to use higher levels of surfactants to achieve the best soil removal performance on polyester blends.

Formulas containing higher alcohol sulfate to LAS ratios are seen to be preferred for cleaning pure polyester (Fig. 14). It is further apparent that higher surfactant levels are preferred. At the under use level in hard water there is a negative value at very high phosphate low surfactant levels (Fig. 15). This extremely poor response is explained as a redeposition problem and provides an insight into the preferential performance for high surfactant systems. Polyester and other hydrophobic fibers have presented a severe challenge to the detergent chemist because of the attraction that these substances have for oily soil. They are difficult to clean and require detergent products with good anti-soil redeposition properties. These formulations' soil suspending properties would be best and, hence, may account for their more desirable performance. Figure 16 and 17 serve to complete our trifunctional set of data and they reaffirm some of the same apparent conclusions made above. Further clarification of the phosphate dependency effect for HMWAS-LAS blends was demonstrated by running a direct comparison of 14% HMWAS-LAS against 20% LAS. Figure 18 illustrates these relative effects.

The conclusions of our detergency work are as follows: (a) Blends of HMWAS and LAS are excellent detergents; (b) HMWAS performs best with higher tripolyphosphate concentrations; (c) hard water affects both HMWAS and LAS; (d) synthetic fabrics require higher surfactant concentrations for best cleaning; (e) under use severely affects the cleaning efficiency on synthetics and synthetic blends; and (f) polyester fabrics are more responsive to small formula changes at normal use levels, necessitating greater proficiency in formula design.

Foam

A great deal of attention is given to the foam profile of a detergent system. This consumer-oriented concern is of considerable importance to the surfactant chemist. The goals of a heavy duty laundry formula are nearly always defined in terms of detergency and foam performance.

HMWAS do not exhibit similar foam characteristics to LAS. Whereas LAS is a higher foamer in hard water than in soft water, HMWAS is a higher foamer in soft water than in hard water. Blends of HMWAS and LAS tend to demonstrate the foam property of the major constituent of the blend. The effect of LAS-HMWAS ratio is shown in Table II in a top-loading washing machine foam test. The numbers are relative values and the higher numbers indicate more foam. We see a normal trend of more foam in the direction of richer LAS blends and higher total active levels. Water hardness acts as a severe foam depressant with high molecular weight alkyl sulfates. This effect is shown in Table III. The elimination of foam in its entirety at the 300 ppm hardness level may suggest itself as a new low foaming heavy duty concept.

The interest in developing detergent systems of potentially commercial value led us to explore the use of available foam boosters to increase the foam level of mixed active HMWAS-LAS formulations. Table IV illustrates the effects of a number of commercial foam boosters on blends of HMWAS and LAS. For reference, we included two commercial detergent products brought from a store shelf and included in this test series. The effect of linear primary synthetic lauryl alcohol as a foam booster with alcohol sulfates has been known and in this work it compares well with other foam stabilizers (Table V). A confirmatory laboratory foam test, based on hand dishwashing, showed the effect of foam boosters on a HMWAS-LAS formulation. The poor foam performance in hard water was again observed and the effects of the foam boosters indicated a number of possibilities for modifying the foam as desired.

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