

The Mixed Surfactant System of Linear Alkylbenzene Sulfonate and Alpha Olefin Sulfonate

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Physicochemical and detergency studies on the mixed surfactant system of linear alkylbenzene sulfonate-sodium salt (LABS) and alpha olefin sulfonate-sodium salt (AOS) have been carried out. The binary surfactant system exhibits minima in the surface tension and in the critical micelle concentration when the two surfactants are present in the ratio 80:20, indicating synergism in the mixed monolayer and in mixed micelles at this proportion of the two surfactants. The mixed micelles improve hard-water tolerance of LABS and reduce the loss of LABS via $\text{Ca}(\text{LABS})_2$ precipitation. Addition of AOS to LABS improves its lime soap dispersion properties. The effect is highly significant when AOS is present at the 20% level in the mixed surfactant system. A synergistic mixture of the two surfactants, when used in phosphate-free, carbonate-built detergent product formulation, exhibits superior detergency, low ash deposit and better stain-removing ability when compared to products containing LABS as the sole active surfactant.

KEY WORDS: Alpha olefin sulfonate, carbonate built detergents, detergency, hand wash, linear alkylbenzene sulfonate, mixed surfactant system, synergy.

Linear alkylbenzene sulfonate-sodium salt (LABS) is the most commonly used active surfactant for laundry products throughout the world (1,2). In comparison with other actives, LABS offers good performance, competitive price and ease of processing. However, in underbuilt products, the efficacy of LABS is significantly diminished in hard water (3). The problem can be circumvented to a significant extent by the use of co-surfactants. The most commonly used co-surfactants are nonionic surfactants (3-5), which have high tolerance for water hardness. Because surfactants vary in their ability to remove different soils from various fabrics, co-surfactants also offer additional advantages in detergency of mixed wash loads (5-7).

The use of nonionics as co-surfactants, because of their high skin-degreasing power, is not desirable in products for hand-wash situations prevalent in India and other developing and third-world countries. For this reason, there is a need to examine other surfactants that are cost-effective, have better tolerance toward water hardness and possess low skin irritancy. Alpha olefin sulfonate-sodium salts (AOS) as a class fulfill these preliminary requirements.

As a part of our studies on mixed surfactant systems, we considered it worthwhile to examine the synergism between LABS and AOS and its effect on performance-related properties. We report here the effect of AOS on the surface tension reduction of water, critical micelle concentration (CMC), lime soap dispersion ability, sensitivity toward water hardness and the detergency of LABS. The purpose of these studies was to investigate the

advantages of LABS-AOS synergism in performance-related properties of prototype phosphate-free carbonate-built formulations predominant in the Indian market. These product formulations do not contain any zeolite and hence differ from the one used by Cox and co-workers in their studies (8).

EXPERIMENTAL PROCEDURES

Materials. Commercial-grade samples of LABS (av. mol. wt = 343) and AOS (av. mol. wt = 350), obtained by sulfonation of LAB (Indian Petrochemicals Limited; $C_{10} = 14$, $C_{11} = 32$, $C_{12} = 37$, $C_{13} = 16$ and $C_{14} = 1\%$) and AO (Shell, Houston, TX; $C_{14} = 2$, $C_{16} = 54$, $C_{18} = 42$, $C_{20} = 1\%$) were used in the present studies. The sodium sulfate and unsulfonated matter content in the two surfactants were: LABS, 2.4% and 1.9%; AOS, 4.3% and 2.6%, respectively.

The concentration of sodium sulfate in all test solutions used for surface tension, critical micelle concentration, lime soap dispersion ability and hardness tolerance studies were maintained at 0.01 M level to approximate the ionic strength of the wash liquor of a typical detergent powder.

Surface tension. The surface tension of aqueous solutions of LABS, AOS and their mixtures were determined by the drop weight method (9). The number of drops in a fixed volume of the surfactant solution was measured with a stalagmometer, and the surface tension was determined. These measurements were made in water that contained no calcium or magnesium.

Critical micelle concentration (CMC). The CMC's of LABS, AOS and their mixtures were determined by the surface tension method.

The surface tension of solutions of varying concentration of the surfactant was determined as described above and plotted against the logarithm of the concentration. The CMC was then obtained from the sharp break in the plot (10). These measurements were made in water that contained no calcium or magnesium.

Lime soap dispersion ability (LSDA). The lime soap dispersion ability was determined at 30°C by following the procedure of Borghetty and Bergman (11). Sodium oleate solution (5 mL of 0.5%) was pipetted into a clean and oven-dried Nestler tube. Varying amounts of the dispersing agent (*viz.* LABS, AOS or their mixtures containing different proportions of the two surfactants) and enough distilled water and 10 mL of 1000-ppm hard water ($\text{Ca}^{++}/\text{Mg}^{++} = 2:1$) were then added to bring the final volume to 30 mL. The ionic strength in the resultant solution was maintained at 0.01M sodium sulfate to approximate the ionic strength of wash liquor. The Nestler tube was then stoppered and inverted 20 times while being returned to the starting position each time. The condition of the lime soap particles was observed. A coagulated precipitate with clear solution between lumps was taken as indicative of an inadequate quantity of dispersing agent in the solution to disperse the lime soap. The

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procedure was repeated with increasing quantities of dispersing agent until coagulation became translucent and lumps were no longer visible. The lime soap dispersing ability was then expressed as the number of grams of surfactant required to disperse the lime soap formed from 100 g of sodium oleate in 333.3-ppm hard water.

Sensitivity toward calcium ions. The effect of AOS on the sensitivity of LABS toward calcium ions was determined by following the procedure described by Cox and co-workers (4). A known volume of the test solution containing 0.1% surfactant (LABS, AOS, or mixture of varying proportions of the two surfactants) was titrated with 0.1% calcium chloride solution to the turbidimetric end point. The concentration of sodium sulfate in each solution was maintained at 0.01M to account for the ionic strength in the wash liquor of typical laundry powder. The pH of each solution was adjusted to approximately 9 with sodium hydroxide, and calcium chloride solution was added slowly at a rate of 0.5–1.0 mL per min. Toward the end point, after each 0.2-mL addition of calcium chloride solution, the titration flask was allowed to stand for 2 to 3 min and checked for turbidity. The volume of calcium chloride solution required to produce a visible turbidity was taken as the measure of the tolerance of the surfactant system toward water-hardness ions.

Detergency. Detergency studies were divided into three parts: soil removal, ash deposit and stain removal. The ash deposit and stain removal studies were confined only to the surfactant system containing 20% AOS (w/w).

Soil removal. The effect of part replacement of LABS by AOS on detergency was determined by evaluating the soil-removing ability of carbonate-built detergent product formulations containing varying proportions of LABS and AOS in the surfactant component of the formulation in 300-ppm hard water ($\text{Ca}^{++}/\text{Mg}^{++} = 2:1$). Two types of fabric, 'white cotton' and 'white polyester-cotton' (50:50 blend), were used in the present studies.

Pretreatment of fabric. The finishing chemicals on the fabric surface were removed by scouring at near-boiling temperature with a 0.2N solution of sodium hydroxide for 45 min (12) (Two liters of solution was used for every meter of fabric subjected to pretreatment.) The fabric was then washed repeatedly with hot water until the washings were free from alkali. It was then soaked with 0.05% solution of poly(nona-)oxyethylated nonyl phenol in distilled water at 80–90°C for 15 min and rinsed with hot and cold distilled water. The test fabric was then dried in a dust-free environment. Scouring with a 0.05% solution of poly(nona-)oxyethylated nonyl phenol in distilled water was then repeated to ensure complete removal of finishing chemicals from the fabric.

Soil. The sample of soil was prepared by mixing thoroughly 2 g of rice bran oil, 1 g of HOWCOCG-3 (a homogeneous stable suspension containing 10% graphite in refined mineral oil), 0.3 g ferric oxide, 2.0 g cement and 0.3 g used motor oil, and dispersing the mass obtained in commercial-grade carbon tetrachloride to a total volume of 100 mL. The soil dispersion thus obtained was applied on the test fabric by using a padding mangle. The soiled fabric was conditioned for 8–10 h in an air oven set at 50°C.

Swatches of 5" × 5" were cut from the soiled fabric, and the reflectance of the soiled fabric and unsoiled reference pieces was measured. The soiled fabric was then washed

with product formulation and the unsoiled reference with plain water under identical conditions, which simulated a hand wash procedure. The test fabric was immersed in a bucket containing wash liquor at ambient temperature. The mechanical working on the fabric was done manually with both hands while keeping the fabric immersed in the wash liquor. On completion of the wash cycle, the fabric was taken out of the wash liquor, squeezed and immersed in another bucket containing plain water for rinsing. The fabric was mildly agitated during this operation. The rinsing operation was repeated 2–3 times by immersing the squeezed fabric into fresh water every time. At the end of rinse cycles, the fabric was squeezed by hand, jerked to remove wrinkles, spread on a rope in a dust-free room and allowed to dry at ambient temperature. The wash parameters and the details of product formulation used are given in Table 1.

The reflectance of the soiled and cleaned swatches and the pretreated unsoiled fabric were measured with a reflectometer (Data Color Model 9133, Hewlett-Packard, Palo Alto, CA) equipped with integrating sphere geometry. A minimum of three readings on the face side of each swatch from different angles were taken for all the swatches. The instrument was calibrated against an internal standard before measuring the reflectance of each swatch. From the reflectance data, K/S ratios were calculated according to the Kubelka-Munk equation:

$$K/S = (1 - R)^2/2R \quad [1]$$

where R is the observed reflectance, K is the coefficient of reflectivity and S is the coefficient of light scattering.

The amount of soil on fabric was expressed as the difference between K/S values after and before soiling or after and before washing:

$$S = \frac{(1 - R_S)^2}{2 R_S} - \frac{(1 - R_i)^2}{2 R_i} \quad [2]$$

TABLE 1

Effect of Partial Replacement of LABS by AOS on Detergency: Wash Parameters and Product Formulation^a

Fabric type	
Cotton (Khadi)	
Polyester-cotton (50:50 blend)	
Wash parameters	
Wash and rinse temperature	35 ± 2°C
Fabric to liquid ratio	1:7
Wash time	10 min
Rinse time	4 × 5 min
Water hardness	300 ppm ($\text{Ca}^{++}/\text{Mg}^{++} = 2:1$)
Drying	In dust-free room at ambient temperature 35–40°C
Product dose	1% wt/vol
Product formulation	
LABS	X%
AOS	10 - X%
Sodium carbonate	50%
Sodium metasilicate	5%
Sodium chloride	5%
Sodium sulfate	20%
Moisture	10%

^aAbbreviations: LABS, linear alkylbenzene sulfonate; AOS, alpha olefin sulfonate.

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$$W = \frac{(1 - R_w)^2}{2 R_w} - \frac{(1 - R_u)^2}{2 R_u} \quad [3]$$

where S = soiling value of the soiled fabric; W = soiling value of the washed fabric; and the average reflectance values, expressed as fractions of 1.00, of the test swatches are: R_i = initial; R_s = after soiling; R_w = after soiling and washing; R_u = after washing without soiling. Average values of S and W calculated for each pair of test swatches were used to calculate percentage soil removal (13).

Ash deposit. The effect of partial (20% w/w) replacement of LABS by AOS in the surfactant system of a carbonate-built product on ash deposit was determined for up to 30 wash cycles on two types of fabrics, *viz.* cotton and polyester cotton (50:50) blend.

The test fabrics were scoured as described above. They were then cut into swatches of $10'' \times 10''$. A bunch of 10 such swatches was subjected to 'wash-rinse-dry' cycles simulating hand-wash conditions described above. The wash parameters and product formulations used in the study are summarized in Table 2. After every three 'wash-rinse-dry' cycles, one of the swatches was removed from the bunch, and the inorganic salt incrustation on fabric was extracted with 0.1N hydrochloric acid (14). The concentration of hardness ions in the extracted solution was determined by standard ethylene diaminetetraacetic acid-di sodium salt (EDTA) titrations, and the results were converted to weight equivalent of calcium carbonate for 100 g of the test fabric by means of an appropriate conversion factor.

Stain removal. The effect of partial (20% w/w) replacement of LABS by AOS in the surfactant system of a carbonate-built detergent product formulation on its ability to remove most common stains, such as tea, blood and turmeric, has been determined on two types of fabric, *viz.* cotton and polyester-cotton (50:50 blend). The pre-ashed fabric obtained after 6, 12, 15 and 18 'wash-rinse-dry' cycles in the ash deposit studies was used for the present

TABLE 2

Effect of Partial Replacement of LABS by AOS on Ash Deposit: Wash Parameters and Product Formulations^a

Fabric type	Cotton, and polyester/cotton (50:50 blend)	
Mode of wash	Hand wash	
Wash and rinse temperature	$35 \pm 2^\circ\text{C}$	
Fabric to liquid ratio	1:7	
Water hardness	300 ppm ($\text{Ca}^{++}/\text{Mg}^{++} = 2:1$)	
Wash time	10 min	
Rinse time	3×5 min	
Drying	In dust-free room at ambient temperature ($35-40^\circ\text{C}$)	
Product concentration	1% (w/v)	
Product formulation		
Ingredients	Control (%)	Experimental (%)
LABS	10	8
AOS	—	2
Sodium carbonate	50	50
Sodium meta silicate (100%)	5	5
Sodium sulphate	20	20
Sodium chloride	5	5
Moisture	10	10

^aAbbreviations: See Table 1.

studies. These fabric pieces were selected to simulate an actual situation because it would be abnormal to expect stains on fabric only when it is brand new.

A known amount (0.2 mL) of the stain sample was gently placed onto the test fabric mounted on an embroidery hoop. The soil was then allowed to spread on the fabric by keeping it in an air oven at 50°C . The reflectances of the stained fabric in and around the stain area were measured. The stained fabrics were then washed under identical hand-wash conditions. The wash parameters and the details of product formulations were identical to those of the ash deposit studies. The reflectance of the washed fabrics in and around the stained area was measured as described above.

RESULTS AND DISCUSSION

The surface tension of 0.05% aqueous solutions of LABS, AOS and binary surfactant system containing varying proportions of the two surfactants is shown in Figure 1. There is a decrease in surface tension when a small amount of LABS is replaced by AOS in the surfactant system. The maximum lowering is observed when LABS and AOS are present in the ratio 80:20 (w/w). The decrease in surface tension lowering on mixing two surfactants is attributed to the strong attractive interactions between the surfactant molecules in the mixed monolayer at the aqueous solution/air interface.

The results of CMC studies are presented graphically in Figure 2. LABS-AOS mixtures rich in LABS have smaller CMC values than LABS alone, indicating that addition of small amounts of AOS tends to promote the formation of micelles in the LABS solution. A minimum in the CMC plot is observed at around 20% AOS, revealing the optimum micelle-promoting tendency of AOS at this proportion.

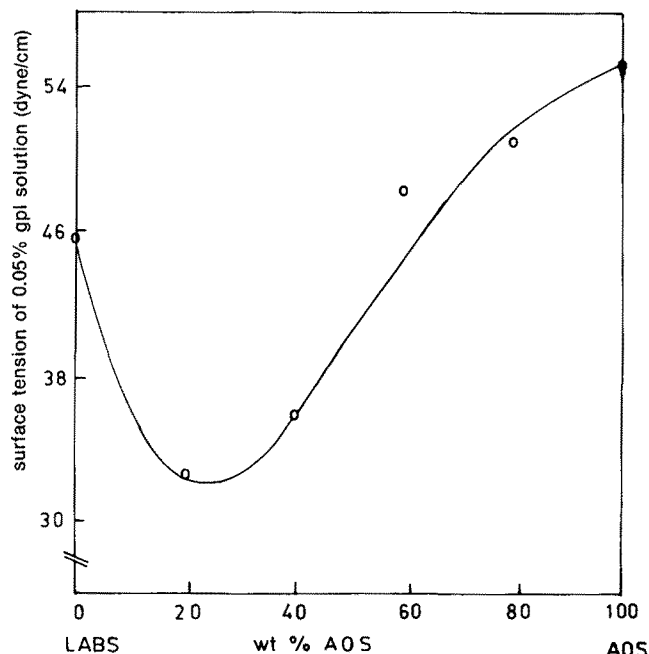


FIG. 1. Reduction in surface tension of 0.05% solutions of linear alkylbenzene sulfonate-alpha olefin sulfonate (LABS-AOS) mixed surfactant system.

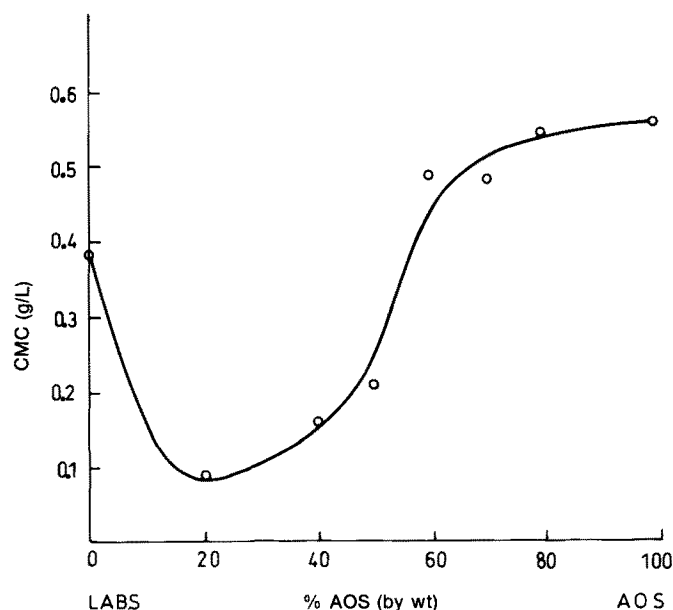


FIG. 2. Critical micelle concentration (CMC) of linear alkylbenzene sulfonate-alpha olefin sulfonate (LABS-AOS) mixed surfactant system.

The decrease in surface tension lowering of aqueous solutions and the minimum in the CMC plot are the consequence of synergism between LABS and AOS in the mixed monolayer and mixed micelles, and this is known to be related to synergism in various performance-related properties (15).

Fabric yellowing, resulting from the deposition of calcium and magnesium salts of fatty acids (lime-soap), has been noticed with the use of LABS-based products where soap provides the builder functions (16) and is attributed to the poor lime-soap dispersion ability of LABS (17). Apart from the soap in the formulation, lime-soap may be formed *in situ* on soiled fabric containing free fatty acids from human sweat sebum soil and fatty soil from domestic dirt. A surfactant system with superior LSDA keeps the lime soap dispersed in the medium and hence prevents the build-up of fatty material on fabric, which may ultimately lead to fabric yellowing, odor, dulling of colored fabric and increased redeposition of soil on the fabric. In an unbuilt/underbuilt wash medium, in the absence of a good lime-soap dispersant, the insoluble lime-soap skin formed around the fatty soil on the fabric is not easily dispersed. It prevents the contact of soil with wash liquor, thereby inhibiting the removal of fatty soil from the fabric and resulting in poor fatty soil detergency.

Figure 3 shows that the LSDA of AOS is superior to that of LABS, and this is in accordance with the published literature (18). We find that a partial replacement of LABS by AOS tends to improve the LSDA, and the effect is more pronounced at the 20 to 30% replacement level. A mixed surfactant system containing synergistic proportions of LABS and AOS is therefore expected to exhibit superior fatty soil detergency.

In an unbuilt or underbuilt wash situation, water hardness ions tend to interact with fabric, soil and surfactant. All these interactions lead to poor detergency. These ions precipitate a part of the anionic surfactant from the wash liquor as insoluble salts, resulting in a decrease in the

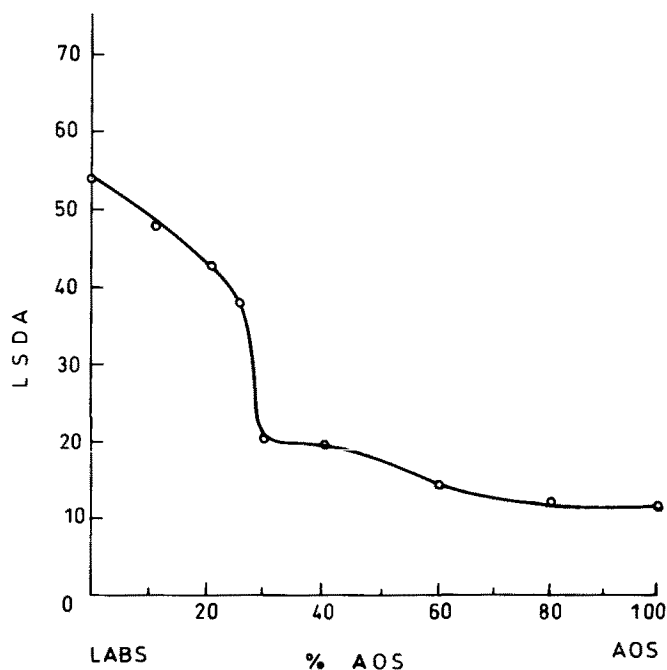


FIG. 3. Lime soap dispersing ability of linear alkylbenzene sulfonate-alpha olefin sulfonate (LABS-AOS) mixed surfactant system. LSDA, lime soap dispersion ability.

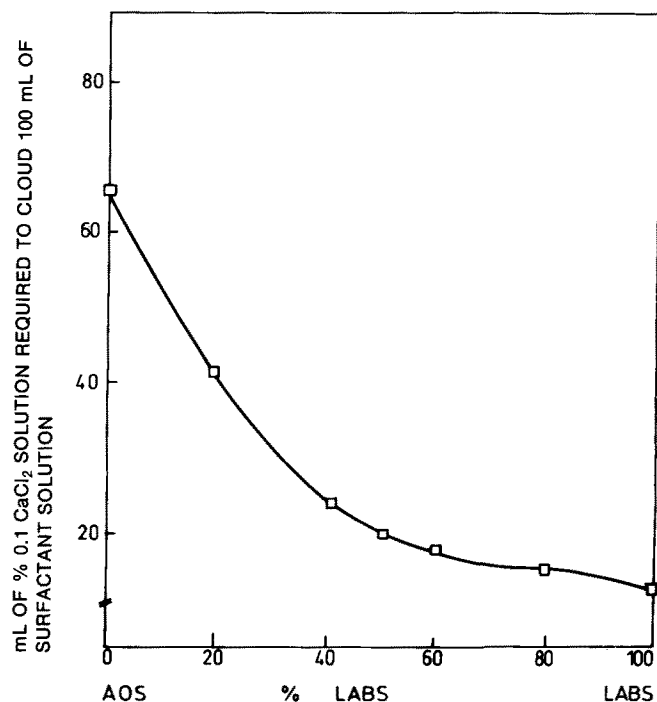


FIG. 4. Resistance of linear alkylbenzene sulfonate-alpha olefin sulfonate (LABS-AOS) mixtures to precipitation by calcium ions at $32 \pm 2^\circ\text{C}$.

concentration of active surfactant available for detergency. The extent of anionic surfactant precipitated is determined by the water hardness ion tolerance of the surfactant.

The effect of the LABS/AOS ratio on calcium sensitivity is shown in Figure 4. Compared to AOS, LABS has poor tolerance for hardness ions. A partial substitution

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of AOS tends to decrease the hardness sensitivity of LABS. This in turn is expected to improve LABS detergency at relatively higher levels of water hardness (4).

The results of detergency studies on cotton and polyester-cotton blend are presented in Figures 5 and 6, respectively. Each data point reported is an average of three independent experiments. When 20–25% of LABS in the product is replaced by AOS, the formulation performed best. Our results are in general agreement with the studies of Cox and co-workers (8).

In view of the synergism in detergency observed for the mixed surfactant system, studies on ash deposit and stain removal were confined to 20% w/w replacement of LABS by AOS. The results of our studies on ash deposit are presented in Figures 7 and 8. During early washes, the rate of ash build-up increases with the increasing number of washes and then tends to settle down to an almost

constant build-up. A similar pattern was observed for both cotton and polyester-cotton, though the absolute value of ash build-up on polyester-cotton was lower than that on cotton. We find that partial replacement of LABS by AOS tends to decrease the ash deposit on both types of fabrics and hence offers distinct advantages over LABS. Ash deposit is considered to be a product negative as it results in apparent graying of white fabric, fading of colored fabrics, and also harshening of the fabric, thereby imparting an uncomfortable feeling to the wearer (19).

The results of our studies on the effect of partial replacement of LABS by AOS on the ability of formulations to remove stains from cotton and polyester-cotton blend are summarized in Table 3. The LABS-AOS (80:20) mixed surfactant system exhibits superior stain removing ability, as compared to LABS alone, from both types of fabrics.

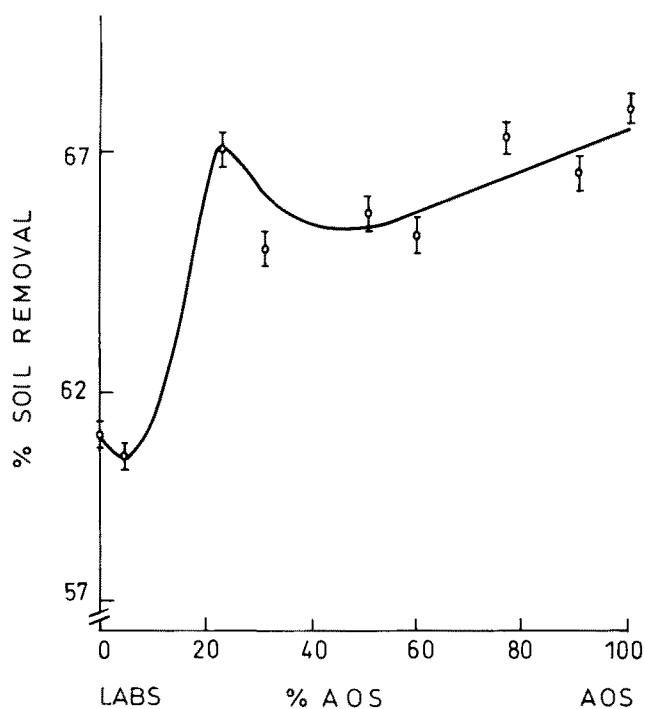


FIG. 5. Effect of partial replacement of linear alkylbenzene sulfonate (LABS) by alpha olefin sulfonate (AOS) in surfactant component of carbonate-built product formulation (Table 1) on detergency of cotton.

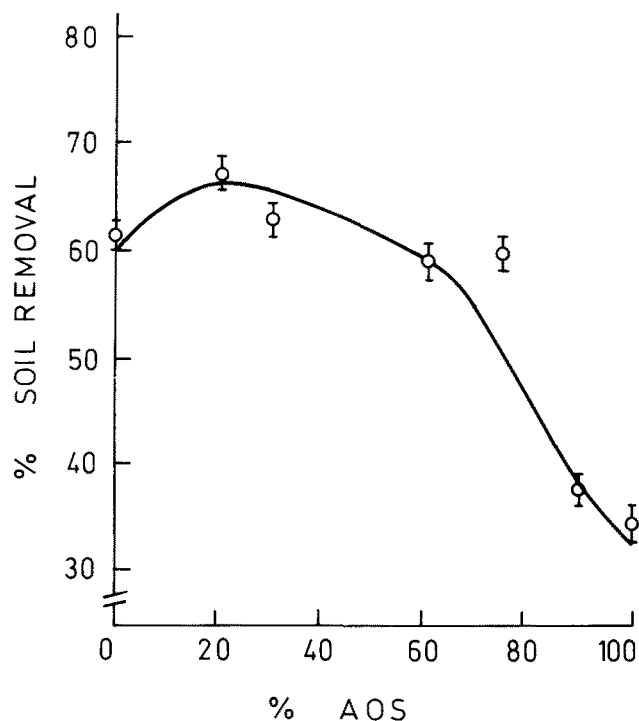


FIG. 6. Effect of partial replacement of linear alkylbenzene sulfonate by alpha olefin sulfonate (AOS) in surfactant component of carbonate-built product formulation (Table 1) on detergency of polyester-cotton (50:50 blend).

TABLE 3

Stain Removal from Cotton and Polyester-Cotton (50:50 blend)

Stain	Number of wash cycles prior to application of stain	Stain removal, ΔR			
		Cotton fabric		Polyester-cotton	
		Control ^a	Experimental ^b	Control ^a	Experimental ^b
Tea	18	16.12	12.19	7.42	6.7
Blood	15	3.57	2.27	2.64	1.62
Blood	6	5.39	3.87	0.86	0.76
Turmeric + milk	12	9.53	4.23	0.82	0.42

^aContaining linear alkylbenzene sulfonate (LABS) as sole active.

^bContaining LABS + alpha olefin sulfonate mixed active system (80:20, w/w).

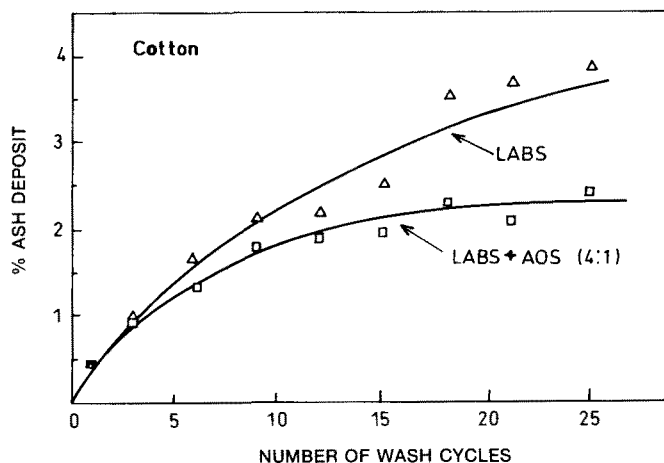


FIG. 7. Ash deposit on cotton (details of product dose, product formulation and wash parameters given in Table 2).

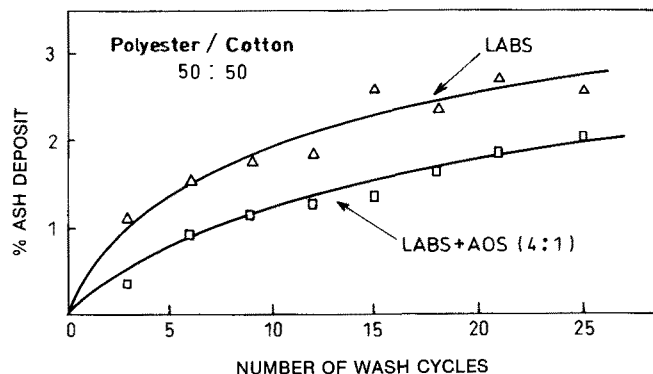


FIG. 8. Ash deposit on polyester-cotton (50:50 blend) (details of product dose, product formulation and wash parameters given in Table 2).

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[Received February 11, 1992; accepted September 30, 1992]