Worldwide Studies of Mixed Active Laundry Detergency

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ABSTRACT

A cooperative study involving laboratories in the United States, Europe and Japan was conducted to investigate the detergency performance of mixed active detergents. Each location tested mixtures commonly manufactured in their region using wash conditions typical of their area. The utility of the data in selecting optimum cost/performance formulations is discussed. Under typical wash conditions found in the United States and Japan, a mixedactive formulation is not required. In most cases, optimum detergency is obtained by a linear alkylbenzene sulfonate (LAS) based formulation. In Europe, a mixed active detergent is required. Although LAS provides optimum performance, some soap (or soap plus nonionic [NI]) must be added to control foam.

INTRODUCTION

The choice of surfactant system for a laundry detergent varies from continent to continent and depends strongly on availability and cost of surfactants and conditions under which they are typically used. Mixed active formulations are popular worldwide because they offer the advantage of good performance over a wider range of wash conditions and allow manufacturers flexibility with respect to surfactant supply and demand. However, different regions of the world use different mixed active systems.

Because of the complexity of investigating mixed active detergents on a worldwide scale, a cooperative study was performed using testing laboratories in the USA, Spain and Japan. Each laboratory tested mixed active formulations commonly used in their region. These surfactant systems included LAS/ES/AS (linear alkylbenzene sulfonate/ether sulfate/alcohol sulfate), LAS/NI (nonionic)/ soap, and LAS/AOS (alpha olefin sulfonate). Each surfactant system was tested under wash conditions typical for that region. The effect of wash temperature, surfactant molecular weight, water hardness, builder type, and cloth/ soil type on the performance of each mixed active system was examined.

EXPERIMENTAL PROCEDURES

Detergency testing was performed using equipment and procedures outlined in Table I. All tests were run in duplicate. In US and Japanese studies, detergency performance was reported as reflectance (in Rd units) of the washed cloth. (Reflectances of the starting soiled cloths were similar and the cloths originated from the same soiling batch.) In the European (Spanish) study, detergency performance was determined by measuring the change (Δ Rd) in reflectance between soiled and washed cloths. In all cases, higher Rd or Δ Rd values indicate better detergency performance.

All locations used sebum-soiled cloth prepared by the US laboratory. Sebum is a blend of fatty acids, natural waxes and oils which represents the soil exuded from human skin (1, 2). The sebum soil used consisted of a 6:1 blend of synthetic sebum and cleaned air conditioner dust. Both sebum-soiled cotton (Testfabrics S/419) and sebum-soiled permanent press (Testfabrics S/7406) cloths were used. The permanent press cloth used was a 65% Dacron/35% cotton blend with a permanent press finish.

The Spain facility also used EMPA 101 cloth (EMPA Institute, St. Gallen, Switzerland) which consists of olive oil/carbon black-soiled cotton.

Metasilicate, which is commonly added as a rust preventative and aids in raising wash-water pH, was not added to the test formulations in order to maximize the effect of surfactant-builder interactions and to minimize the number of test variables. However, in studies not reported here, the addition of metasilicate was found to enhance performance, particularly formulations containing predominantly LAS. Consequently, practical studies should include silicate as an ingredient in detergent test formulations.

The detergency of each ternary mixed active system was evaluated using 10 different surfactant blends, as illustrated in Figure 1. These ten formulations contain

TABLE I

	Laboratory		
	United States	Spain	Japan
Detergency testing apparatus	Terg-O-Tometer	Launder-Ometer ^a	Terg-O-Tometer ^b
Wash cycle	10 min	20 min	10 min
Rinse cycle	5 min	Hand rinse	Two 3-min
Wash temperature	60, 100, 140 F	100, 140 F	60, 100 F
Temperature of rinse water	Same as wash water	Room temperature	Same as wash water
Water hardness	50, 150 ppm	150, 300 ppm	50 ppm
Number soiled cloths (3-in. by 4½-in.)	6	3	6
Number unsoiled cloths (as ballast)	3	0	3

^aModel B-5 (Type LHD-HT), Atlas Electric Device Company, USA. ^bModel 7243, United States Testing Company, USA.



FIG. 1. Triangular plot showing the composition of the 10 surfactant blends tested.



FIG. 2. Example of computer-generated triangular performance contour plot (for dodecyl-LAS/ C_{12} - $_{18}$ [40% EO] ES/ C_{12} - $_{18}$ AS formulations [0.15% use level] with carbonate builder at 50 ppm water hardness, 100 F (38 C), using sebum-soiled cotton cloth).



FIG. 3. Triangular performance plot showing optimum detergency zone and regions of secondary performance (from data shown in Fig. 2).

a constant total active and a constant amount of builder. As shown, these ten formulations represent a complete cross-section of all possible combinations of the three surfactants.

To illustrate detergency trends, triangular performancecontour plots were constructed using a Simplex optimization computer program (3). An example is given in Figure 2. The detergency performance (in Rd units) is given for each surfactant mixture tested. The Simplex optimization program determines what surfactant mixtures give equivalent performance with a 0.5 reflectance unit range (with sebum soil). In this example, the best performing mixture is the all-LAS formulation. Mixtures performing with 0.5 Rd units of the all-LAS formulation include the 9% LAS/3% ES/3% AS and the 7.5% LAS/7.5% ES blends. All other mixtures the Simplex program estimates (based on the performances of the other mixtures) will also fall into this detergency zone. This area of highest equivalent detergency performance will be referred to as the "optimum detergency zone." The computer program also calculates regions of poorer detergency, as shown in Figure 2.

In most detergency tests, a difference of 0.5-1.0 reflectance units is considered significant (for sebum-soiled cloth) at the 95% confidence limit. Although the uncertainty in detergency data varies from test to test, a difference of 0.5 Rd units was used in preparing the triangular performance contour plots, since their purpose is to illustrate detergency trends and not to represent absolute maxima.

When EMPA cloth was used, a difference of 2-3 Rd units was found to be significant, based on a 95% confidence limit. Consequently, detergency contour plots of EMPA cloth data were constructed using a difference of 2.0 Rd units.

In the following text, performance plots will show the optimum detergency zone and, in most cases, secondary performance zones. An example using the previous plot (Fig. 2) is shown in Figure 3.

RESULTS AND DISCUSSION

Part of the cooperative study involved each laboratory running identical tests to determine lab-to-lab reproducibility. Figure 4 shows the detergency results obtained by each laboratory using the previously described LAS/ES/ AS formulations with phosphate builder on sebum-soiled cotton at 100 F (38 C). In all studies, at low (50 ppm) water hardness, the optimum detergency zone always includes mixtures high in LAS content. At 150 ppm water hardness, optimum detergency is obtained from LAS/ES blends high in ES content. Although some differences in the sizes of the optimum detergency zones are evident, similar detergency trends were obtained by each laboratory. Minor differences are expected due to differences in test methodology.

The detergency results obtained by each laboratory are discussed below. Each section includes a brief discussion which identifies the mixed active systems and wash conditions used in each area. The effects of water hardness, wash temperature, builder type, cloth type and surfactant molecular weight on the detergency performance of each surfactant mixture are then examined. The utility of the data in determining the optimum cost/performance formulation is discussed.

UNITED STATES MIXED ACTIVE DETERGENTS

A variety of different surfactants is used in laundry powders in the USA, including LAS, ES, AS and NI. Table II gives the 1982 consumption of each of these actives in US heavy-duty powders (HDP). Mixed active products consist primarily of anionic surfactant blends, the most common being a mixture of LAS, ES and AS. Phosphate is the most common builder, particularly in high-performance products. Sodium carbonate is also used, primarily in areas where phosphate use is limited.

A normal wash load in the USA contains mostly synthetic fabrics. The average wash temperature is ca. 100 F (38 C), and the current trend is towards even cooler temperatures for both energy conservation and for protection of fine fabrics. Typical water hardness varies, but the majority

TABLE II

1982 Consumption of Major Surfactants Used in the USA, Europe and Japan

Surfactant	Consumption (Thousand Metric Tons)		
	USA	Europe	Japan
LAS	126	215	77
ES	27	119	25
AS	26	107	12
NI	22	22	4

of households have a water hardness below 150 ppm. The average recommended use level of detergents is ca. 0.15%.

LAS/ES/AS Detergency

LAS/ES/AS detergency was examined using the surfactants and test conditions shown in Table III.

TABLE III

US LAS/ES/AS Detergency Study-Surfactants and Test Conditions

Surfactants

LAS: Dodecylbenzene sulfonate (NALKYLENE[®] 550L LAS)

- AS:
- C_{12} linear alcohol blend (23% C_{12} + 24% C_{14} + 30% C_{16} + 23% C_{18} blend) sodium salt C_{12} linear alcohol blend (same as above) with 40% ethylene oxide sodium salt ES:

Test Conditions

Formulation:	15% total active + 30% builder
Temperatures:	60, 100, and 140 F (16, 38 and 60 C)
Use level:	0,15%
Water hardnesses:	50 and 150 ppm
Soil:	Sebum
Cloth:	Cotton and permanent press



study (for dodecyl-LAS/ C_{12} - $_{18}$ [40% EO] ES/ C_{12} - $_{18}$ AS formulations [0.15% use level] with phosphate builder at 100 F [38 C], using sebum-soiled cotton cloth, at 50 and 150 ppm water hardness).



FIG. 5. Detergency performance of LAS/ES/AS mixtures as a function of temperature on sebum-soiled permanent press cloth (using dodecyl-LAS/ C_{12} - $_{18}$ [40% EO] ES/ C_{12} - $_{18}$ AS formulations [0.15% use level] with phosphate builder).



FIG. 6. Detergency performance of LAS/ES/AS mixtures as a function of temperature on sebum-soiled cotton cloth (using dodecyl-LAS/ C_{12} - $_{18}$ [40% EO] ES/ C_{12} - $_{18}$ AS formulations [0.15% use level] with phosphate builder).

The effect of both temperature and water hardness on the detergency performance of phosphate-built (sodium tripolyphosphate) formulations using sebum-soiled permanent press cloth is shown in Figure 5. At 60 F (16 C) and low (50 ppm) water hardness, the optimum detergency zone is centered towards the all-LAS formulation. As temperature is increased to 100 F (38 C) the optimum detergency zone expands to include nearly all actives. At 140 F (60 C) mixtures high in LAS and alcohol sulfate perform best. This shift in the location of the optimum detergency zone is due to the relatively poor solubility of alcohol sulfate at cooler temperatures. Only at higher temperatures does the detergency performance of alcohol sulfates become significant. Formulations high in LAS content remain in the optimum detergency zone regardless of temperature.

At 60 F with higher (150 ppm) water hardness, the optimum detergency zone centers around LAS/ES mixtures. As temperature is increased, the optimum detergency zone again shifts to include mixtures containing more alcohol sulfate. The extent of this shift is less than was observed at low hardness since alcohol sulfates, although improved by temperature, are also more sensitive to water hardness.

Nearly identical trends are observed with cotton cloth, as shown in Figure 6.

Since 30% phosphate (at 0.15% use level) can only sequester ca. 120 ppm water hardness, the differences in performance at 50 ppm and 150 ppm water hardness represent the difference between a sufficiently built formulation and an underbuilt formulation. A builder level of 30% was chosen to better examine differences in performance between built and underbuilt systems. As shown in Figures 5 and 6, at low hardness (or in sufficiently built systems) optimum detergency is most often centered around the all-LAS formulation. In underbuilt conditions at high hardness, an LAS/ES blend is best.

The effect of LAS molecular weight on the detergency performance of LAS/ES/AS mixtures was examined using both a dodecyl (C_{12} -average) and a tridecyl (C_{13} -average) LAS. LAS molecular weight was found to have little effect on the location of the optimum detergency zone, but it did have a small effect on the overall detergency of LAScontaining formulations, particularly on permanent press cloth. At low water hardness, the higher molecular weight LAS (tridecyl) showed a slight performance advantage over dodecyl LAS. The opposite trend was evident at higher hardness. Previous studies have shown that a tridecyl LAS is best for detergency, but it is also slightly more sensitive to higher water hardness (4).

The effect of \vec{ES} and AS molecular weight on detergency was examined by testing lauryl ($C_{12^{-}14}$) and tallow ($C_{16^{-}18}$), alcohol sulfates and alcohol ether sulfates. The optimum molecular weight depends strongly on temperature and hardness. Higher molecular weight materials perform better at higher temperatures but are more susceptible to higher water hardness.

The effect of builder type was examined by comparing the performance of phosphate-built LAS/ES/AS formulations with those built with sodium carbonate, as shown in Figures 7 and 8. The reflectance range is given for each optimum detergency zone in order to compare overall detergency performance between builders. As shown by the reflectance ranges given, phosphate is the best overall builder. Theoretically, the capacity to remove water hardness (per weight of builder) of sodium carbonate exceeds that of phosphate, but its mechanism for hardness removal is less efficient. Phosphate sequesters hardness quickly whereas sodium carbonate removes hardness by forming



FIG. 7. Detergency performance of LAS/ES/AS mixtures with phosphate (STPP) and sodium carbonate builders on sebum-soiled permanent press cloth (using dodecyl-LAS/ C_{12} - $_{18}$ [40% EO] ES/ C_{12} - $_{18}$ AS formulations [0.15% use level] at 100 F [38 C]).



FIG. 8. Detergency performance of LAS/ES/AS mixtures with phosphate (STPP) and sodium carbonate builders on sebum-soiled cotton cloth (using dodecyl-LAS/ C_{12} -18 [40% EO] ES/ C_{12} -18 AS formulations [0.15% use level] at 100 F [38 C]).

insoluble calcium and magnesium carbonates. The latter process is relatively slow and never totally removes all of the hardness which results in poorer detergency performance.

Locations of the optimum detergency zones with carbonate builder are similar to those obtained with phosphate. However, in most cases, the optimum detergency zones obtained using carbonate are smaller than those obtained with phosphate. Smaller zones are the result of a larger range in the detergency performances observed for the various surfactant mixtures.

Optimization of LAS/ES/AS Detergancy

The data previously described are useful in determining the best performing mixture for a given set of conditions. For example, assume the following criteria are important in the development of a laundry product potentially containing an LAS/ES/AS active: (a) cold (60 F) water performance; (b) detergency on sebum soil; (c) built with phosphate.

Figure 9 shows performance curves fitting the above criteria. As shown in the center plot, overlap of the four optimum detergency zones occurs at a region between an 11% LAS/4% ES active and a 7.5% LAS/7.5% ES active.

Since LAS is traditionally the least expensive surfactant, an LAS/ES blend would contain as high an LAS-to-ES ratio as possible, so the 11/4 LAS/ES formation would be the optimum choice.

The criteria described above assume that performance on cotton and performance on permanent press cloths are of equal importance. In reality, the trend in the USA is towards more synthetics, making performance on permanent press cloth more important. If only permanent press cloth is considered, overlap of the optimum detergency zones obtained at 50 to 150 ppm would occur between the all-LAS formulation and the 11/4 LAS/ES mixture. When surfactant costs are considered, the optimum cost/ performance formulation would contain an all-LAS active.

EUROPEAN MIXED ACTIVE DETERGENTS

Nearly all European laundry detergents contain mixed active systems, the most popular being LAS/NI/soap. The estimated 1982 consumptions of LAS, NI, AS and soap for HDP in Europe are given in Table II.

Soap is added to suppress foam because of the prevalance of horizontal-drum washing machines. This type of machine requires controlled (low) foaming detergents, which maintain a low foam profile over a wide range of



FIG. 9. Example of how performance data can be used to optimize surfactant composition (triangular performance curves obtained with dodecyl-LAS/ C_{12} - $_{18}$ [40% EO] ES/ C_{12} - $_{18}$ AS formulations [0.15% use level] with phosphate builder at 60 F [16 C], 50 and 150 ppm water hardness, on sebum-soiled permanent press and cotton cloths and triangular plot [center] showing where optimum detergency zones overlap).

temperatures during the wash cycle. Most products contain phosphate, although the use of carbonate and zeolite builders is spreading in some European countries.

European wash conditions differ greatly from those in the USA. The average wash temperature is substantially higher (greater than 60 C), but, like the USA, the average temperature is dropping due to rising energy costs (5). Typical European water hardness and use level are also higher, averaging ca. 120-240 ppm and 0.5 to 0.75%, respectively. The average wash load also contains significantly more cotton fabrics than typically found in the USA.

LAS/NI/SOAP Detergency

LAS/NI/soap detergency was studied using the surfactants and test conditions listed in Table IV.

The performance of LAS/NI/soap mixtures on EMPA 101 cloth (olive oil/carbon black-soiled cotton) is shown in Figure 10. Under normal European wash conditions (0.5% use level, 60 C, 150 ppm water hardness), as shown in Figure 10A, optimum detergency occurs with two separate sets of mixtures: LAS and LAS/soap mixtures and mixtures high in nonionic content. Other intermediate mixtures, such as LAS/NI, LAS/NI/soap, and NI/soap formulations give poorer performance. This indicates that mixtures of anionic (LAS and soap) and nonionic surfactants are not best for cleaning oily soils, such as EMPA.

Figure 10B shows the effect of lowering the wash temperature to 38 C. Overall performance was observed to decrease by ca. 4 units in the Δ Rd range of the optimum detergency zone. The formulation least affected by the lower temperature is the LAS/soap mixture, whereas the all-nonionic and all-soap formulations showed the largest decrease in performance. This results in a shift in the optimum detergency zone to LAS/soap mixtures having

TABLE IV

European LAS/NI/Soap Detergency Study-Surfactants and Test Conditions

Surfactants

- LAS: Dodecylbenzene sulfonate (PETRELAB[®] 550 LAS)
- NI: C_{12¹⁴} linear alcohol blend with 60% ethylene oxide (Alfonic[®] 1412-60 NI)

Soap: LIRESA tallow soap

Test Conditions

Formulations:	15% total active + 30% phosphate builder
Temperatures:	38 and 60 C (100 and 140 F)
Use Level: Water hardnesses: Soil/cloth:	0.5% 130 and 300 ppm Sebum-soiled cotton EMPA 101 (olive oil/carbon black-soiled cotton)

a higher soap content and the elimination of the optimum detergency zone centered around mixtures high in nonionic content.

The effect of higher (300 ppm) water hardness is shown in Figure 10C. Since a use level of 0.5% gives the phosphatebuilt formulations a theoretical sequestration capacity of ca. 400 ppm, one would not expect a large difference between performance at 150 and 300 ppm water hardnesses. As expected, the increase in water hardness does not affect location of optimum detergency zone. However, overall detergency performance was observed to decrease by ca. $2 \Delta Rd$ units.

The performance of LAS/NI/soap mixtures on sebumsoiled cotton is shown in Figure 11. Under normal European wash conditions (Fig. 11A), optimum detergency performance is obtained by all mixtures except those high



FIG. 10. Detergency performance of LAS/NI/soap formulations (0.5% use level) with phosphate builder on EMPA 101 cloth at (A) 60 C (140 F), 150 ppm water hardness, (B) 38 C (100 F), 150 ppm water hardness, and (C) 38 C (100 F), 300 ppm water hardness (using dodecyl-LAS/ C_{12}^{-14} [60% EO] NI and tallow-based soap).

in soap content. Unlike performance on EMPA 101, the LAS/NI mixture performs as well as the all-LAS and all-NI formulations.

As shown in Figure 11B, lowering wash temperature to 38 C has little effect on the location of the optimum detergency zone.

At 300 ppm water hardness (Fig. 11C), optimum detergency is centered around LAS/NI/soap blends. The slight drop-off in performance of the all-LAS formulation and formulations having a high NI content is not understood but, apparently, all three surfactants work synergistically under very high water hardness conditions.

The effect of nonionic molecular weight was examined using a tallow range $(C_{16}-_{18})$ alcohol with 65% EO. Lauryl range $(C_{12}-_{14})$ nonionic gave slightly superior performance. However, tallow range nonionic is predominantly used in European HDP because the cost of tallow alcohol is sufficiently less than lauryl alcohol to give it a cost/performance advantage.

Optimization of LAS/NI/Soap Detergency

The significance of the detergency results observed with one soil over the other is strictly a matter of choice, based on what soil is judged to represent best the soil which the consumer is concerned with cleaning. EMPA cloth is commonly used in Europe, whereas sebum soil is popular in the USA and Japan. For purposes of discussion, the significance of results obtained with each soil are considered equal.

Figure 12 shows the overlap of the optimum detergency zones observed under typical European wash conditions using sebum-soiled cotton and EMPA cloth. As shown, overlap occurs in two regions; one centered around LAS and LAS/soap formulations, and the other around mixtures high in NI content. Although mixtures from both overlap regions will provide optimum performance, mixtures high in NI are not desirable due to the relatively high cost of nonionic. In addition, the foaming characteristics of a surfactant blend must be considered since front-loading, horizontal-tub washing machines are principally used in Europe. Nearly all European HDP contain soap to control foam. Soap accomplishes this by preferentially binding with hardness ions which reduces the stabilizing effect residual hardness on LAS foam (6). However, by this very process, soap forms insoluble calcium and magnesium salts which can precipitate and build up on fabric, particularly at high water hardness. (Single-cycle detergency testing would not show this.) Consequently, soap content should be minimized.

Considering performance (Fig. 12), cost, and foam performance, a formulation consisting of primarily LAS with a minimum of soap to reduce foam would provide optimum cost/performance. Since nonionic is a relatively low-foaming surfactant, it could be added (at a higher cost) to help reduce the amount of soap needed to control foam. This is the basis for many European LAS/NI/soap formulations. European hand-washing products, which do not require controlled foam, typically contain an all-LAS active.

It should also be mentioned that the trend towards lower wash temperatures in Europe will reduce the level of soap (or nonionic) needed to lower foam since foaming is temperature-dependent.

JAPANESE MIXED ACTIVE DETERGENTS

Japanese laundry detergents employ a variety of surfactant systems including mixtures of LAS, ES, AS and AOS. The 1982 consumption of each of these surfactants for Japanese HDP is given in Table II.

Approximately 80-90% of today's Japanese laundry powders contain zeolite (type A) builder. The remaining HDP contain phosphate.



FIG. 11. Detergency performance of LAS/NI/soap formulations (0.5% use level) with phosphate builder on sebum-soiled cotton cloth at (A) 60 C (140 F), 150 ppm water hardness, (B) 38 C (100 F), 150 ppm water hardness, and (C) 38 C (100 F), 300 ppm water hardness (using dodecyl-LAS/C₁₂-14 [60% EO] NI and tallow-based soap).



FIG. 12. Optimization of LAS/NI/soap composition (overlap of optimum detergency zones obtained with dodecyl-LAS/ C_{12} -14 [60% EO] NI/tallow-based soap formulations [0.5% use level] with phosphate builder at 60 C [140 F], 150 ppm water hardness on sebum-soiled cotton and EMPA 101 cloths).

Japanese washing conditions are unique and differ greatly from those found in Europe and the USA. Typical water hardness is very low (50 ppm or below). The average washing temperature is also lower, ranging from ca. 13 C (60 F) to 38 C (100 F). The average use level (0.12-0.15%) is approximately the same as used in the USA, although a typical wash load in Japan consists more of a 50/50 blend of cotton and noncotton fabrics.

LAS/ES/AS Detergency

LAS/ES/AS detergency was examined using the surfactants and test conditions shown in Table V. Because the typical water hardness in Japan is low, detergents normally contain more active and less builder than those found in the USA and Europe. Consequently, tests were run on formulations containing 25% total active with 20% builder. The performance of LAS/ES/AS mixtures under typical Japanese washing conditions is shown in Figure 13 for both phosphate-built and zeolite-built formulations. With phosphate formulations on permanent press cloth, optimum detergency is obtained with mixtures high in LAS content and with intermediate mixtures containing all three surfactants. On cotton cloth, optimum detergency is centered around LAS/ES mixtures. These results are similar to those observed under typical US washing conditions.

With zeolite-built formulations, significant changes occur in performance. Overall detergency diminishes particularly on permanent press cloth. The optimum detergency zone, which characteristically centers around the all-LAS formulation in phosphate-built mixtures, is now shifted towards LAS/ES blends and the all-ES mixture. The opposite trend is observed on cotton, where optimum

TABLE V

Japanese LAS/ES/AS Detergency Study-Surfactants and Test Conditions

Surfactants

- LAS: Tridecylbenzene sulfonate (NALKEN[®] 6 LAS)
- AS: C14-15 alcohol sulfate-sodium salt (OXOCOL 1415 AS)
- ES: C_{14⁻15} cther sulfate-1.5 mol ethylene oxide (OXOCOL 1415 ES)

Test Conditions

Formulation:	25% total active + 20% builder
Temperatures:	16 and 38 C (60 and 100 F)
Use level:	0.133%
Water hardnesses:	50 ppm
Soil:	Sebum
Cloth:	Cotton and permanent press



FIG. 13. Detergency performance of LAS/ES/AS mixtures under typical Japanese wash conditions with phosphate and zeolite builders (20% builder, 0.133% use level)(using 25% total active formulations with tridecyl-LAS, C_{1415} [1.5 mol EO] ES, C_{1416} AS; at 16 C [60 F] and 50 ppm water hardness on sebum-soiled permanent press and cotton cloths).

detergency is obtained by LAS/AS and LAS/ES blends and by formulations high in LAS and ES content. These differences are largely the result of differences in wash-water pH. Raising the pH of the wash liquor generally improves detergency, particularly on sebum soil. Since phosphate supplies alkalinity, while zeolite does not, the differences observed here are unrealistic since wash-water pH is normally controlled by addition of metasilicate. Additional studies by the US laboratory show that there is little difference between detergency performance of phosphate-built and zeolite-built formulations under typical Japanese wash conditions when metasilicate is added. Overall detergency is slightly diminished, primarily because of zeolite's slightly poorer efficiency in removing water hardness. However, as with phosphate builder, optimum detergency is obtained using an all-LAS or LAS/ES formulation.

Optimization of LAS/ES/AS Detergency

Because Japan's typical wash conditions are very specific, optimization is simple. LAS provides otpimum performance and is the least costly surfactant. Under Japanese wash conditions, an all-LAS active clearly gives optimum cost/ performance.

LAS/AOS Detergency

The detergency performance of LAS/AOS mixtures was examined using commercial C_{14} - C_{18} AOS. The surfactants and test conditions employed were the same as those described in Table V. Results of detergency testing using 25% total active plus 20% phosphate formulations are shown in Figure 14. Optimum performance is obtained with the all-LAS formulation on cotton and the 20/5 LAS/AOS blend on permanent press cloth. Overall detergency performance drops significantly as LAS is replaced with AOS, especially on permanent press cloth.

Identical tests performed using 20% zeolite instead of phosphate. Overall detergency performance decreased in comparison to the phosphate-built formulations. With both cotton and permanent press cloth, the 20/5 LAS/AOS formulation performed best. The synergistic effect of the 20/5 LAS/AOS blend was also more pronounced with zeolite builder.

The effect of temperature was also examined by repeating the detergency tests at 38 C. Although 38 C (100 F) is somewhat higher than typical Japanese wash temperatures, higher temperature was shown to improve REFLECTANCE(Rd)



FIG. 14. Detergency performance of LAS/AOS mixtures as a function of LAS-to-AOS ratio (using 25% total active tridecyl-LAS/ C_{14} - $_{18}$ AOS formulations [0.133% use level] with 20% phosphate builder at 16 C [60 F], 50 ppm hardness on sebum-soiled permanent press and cotton cloths).

overall performance and reduce the differences in performance observed between various LAS/AOS blends.

The effect of LAS molecular weight was also examined. Tridecyl LAS was observed to have a slight performance advantage over dodecyl LAS.

Optimization of LAS/AOS Detergency

Based strictly on performance, the best LAS/AOS/phosphate formulation (under Japanese wash conditions) would contain 20-25% LAS and 5-0% AOS. With zeolite builder, the optimum formulation would be the 20% LAS plus 5% AOS mixture.

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