*Effect of Carbon Chain and Phenyl Isomer Distribution on Use Properties of Linear Alkylbenzene Sulfonate: A Comparison of 'High' and 'Low' 2-Phenyl LAS Homologs

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ABSTRACT

Phenyl isomer distributions, within current commercial limits of HF and $AlCl_3$ linear alkylbenzene sulfonates (LAS), have little effect on dishwashing performance in light-duty liquids (LDL), detergency performance in heavy-duty powders (HDP), and interfacial tension value. The most important factor in determining performance differences among commercial LAS samples is carbon chain homolog distribution. Both HF and $AlCl_3$ LAS perform equally well and can be used interchangeably in high-performance products. The optimum for foam stability in light-duty liquids shifts towards shorter alkyl chain length as water hardness increases. At 0 ppm water hardness the optimum occurs at C_{13}; at 50-150 ppm the optimum moves to C_{11} and C_{12}; and above 150 ppm the optimum shifts to include C_{10}, C_{11} and C_{12}. The detergency performance optimum range in a phosphate built heavy-duty powder at 50 and 150 ppm water hardness includes the C_{12}, C_{13} and C_{14} alkyl chain lengths. In a nonphosphate built powder the optimum is similar at 50 ppm hardness to that of a phosphate built powder, but shifts at 150 ppm hardness to include C_{11}, C_{12} and C_{13}.

INTRODUCTION

Linear alkylbenzene sulfonate (LAS) is the largest-volume surfactant used in household detergent products in the world (1). There are two major processes for producing LAS, which differ primarily in the catalyst system employed. These two processes give different phenyl isomer distributions in the LAS produced. These distributions are compared in Table I.

TABLE I

Typical Phenyl Isomer Distributions for $AlCl_3$ and HF LAS of $C_{11.5}$ Average Molecular Weight

	Phenyl isomer				
LAS	2ϕ	3ϕ	4ϕ	5ϕ	6ϕ
HF	19	20	20	21	20
$AlCl_3$	29	22	18	16	15

The high 2-phenyl product is ca. 30% 2-phenyl isomer, 20% 3-phenyl isomer, and then gradually tapers off to ca. 15-16% of the 5- and 6-phenyl isomers. The low 2-phenyl material is a flatter distribution, with all isomers present at about the same level of ca. 17-21%.

There are widespread opinions in the detergent industry about the comparative performance and formulation characteristics of high versus low 2-phenyl LAS (2). Differences which were noticed were attributed to the phenyl isomer distribution and in some cases this has led to misconceptions. The purpose of this work, which focuses on performance properties only, is to determine precisely how foam stability in dishwashing liquids or laundry powders and detergency in laundry powders are affected by changes in the carbon chain length and phenyl isomer distribution of the LAS.

EXPERIMENTAL

The samples used in this study are individual LAS homologs ranging in carbon chain length from C_{10} through C_{14}. Samples were prepared in the laboratory by the $AlCl_3$ process and by the HF process. This was to ensure that all samples would be similar in salt and free-oil content. The average 2-phenyl content of the $AlCl_3$ homologs was ca. 28-30%, while the average 2-phenyl content for the HF homologs was ca. 17-19%.

The dishwashing tests in this study were run according to Conoco CSL Lab Method No. 311-74. The experimental conditions included hardness levels at 0, 50, 150 and 300 ppm. Tests for light-duty liquids (LDL) were run at 115 F with a formulation concentration of 0.05%, while tests for heavy-duty powders (HDP) were run at 77 F at a concentration of 0.15%. This Conoco lab method is similar to CSMA Test Method No. DCC-10 (3). The LDL formulation selected for testing the homologs was 24% LAS/6% ether sulfate/2% amide. This formulation was selected not only because it is an optimum for an LAS/ether sulfate dishwashing formulation, but also because it would be sensitive enough to reflect any differences between the types of LAS. The ether sulfate was ALFONIC 1412-A® ether sulfate, and the amide was lauric/myristic monoethanol amide (LMMEA). The HDP formulation was 17% LAS/25% sodium tripolyphosphate (STPP).

Interfacial tension studies were run using the spinning drop technique on the same formulations and the same soil conditions as the dishwashing tests. The soil used for both dishwashing and interfacial tension measurements was KEEN vegetable shortening.

The detergency tests were run according to Conoco CSL Lab Method No. 303-74. The experimental conditions included 50 and 150 ppm hardness at 100 F temperature with a use concentration of 0.15%. These tests were run on both sebum and oily soils. Two laundry product formulations were selected for these tests. The phosphate HDP was 16% LAS/30% sodium tripolyphosphate/10% silicate. The nonphosphate HDP contained 12% LAS/4% low mole ether sulfate (LMES)/20% carbonate/20% silicate. These would be similar to many LAS-based, heavy-duty powder formulations and also would be sensitive to differences between the two types of LAS. The Conoco detergency lab method is similar to ASTM Method No. D3050-75 (4).

FOAM STABILITY

The bulk of the foam stability work focused on light-duty liquids. Some work was also done on heavy-duty powders. Although the emphasis on high foam in laundry powders in the USA has diminished from 20 years ago, there are areas in the world where high foam is still a very important factor in the marketing of laundry products.

The results of the dishwashing studies on LDL are summarized in Figures 1-11. A few comments on the way the data are plotted are in order here. In Figures 9 and 10 the values plotted are averaged total plate counts. In Figures 1-8 and 11, however, the plate count for the poorest performer (in most cases, the C_{14} homolog) was arbitrarily set at zero. The plate count values for the other four homologs

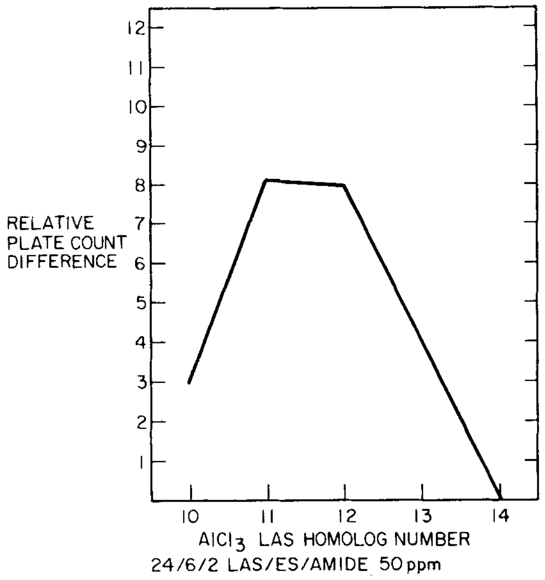

FIG. 1. Foam stability of $AlCl_3$ LAS homologs at 50 ppm water hardness.

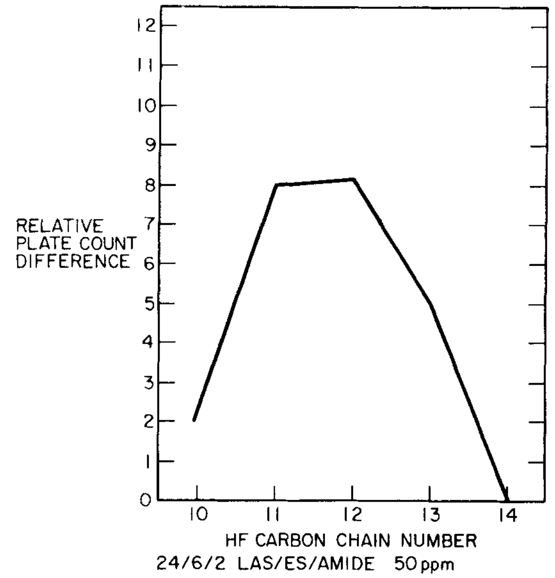

FIG. 2. Foam stability of HF LAS homologs at 50 ppm water hardness.

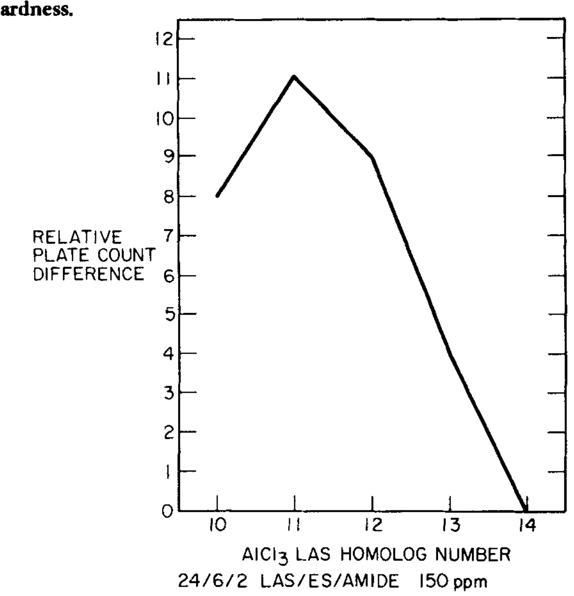

FIG. 3. Foam stability of $AlCl_3$ LAS homologs at 150 ppm water hardness.

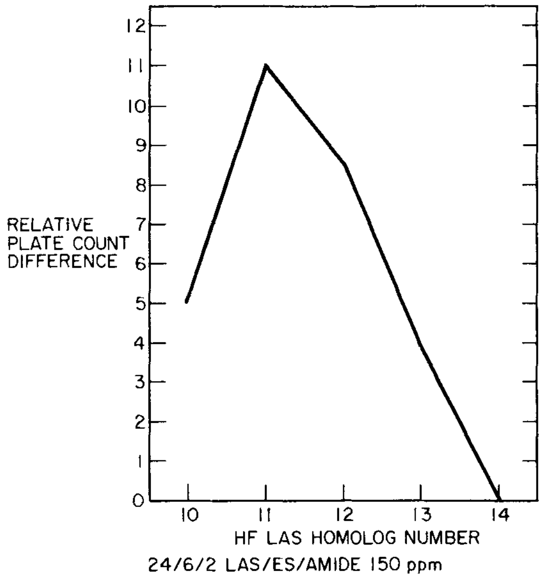

FIG. 4. Foam stability of HF LAS homologs at 150 ppm water hardness.

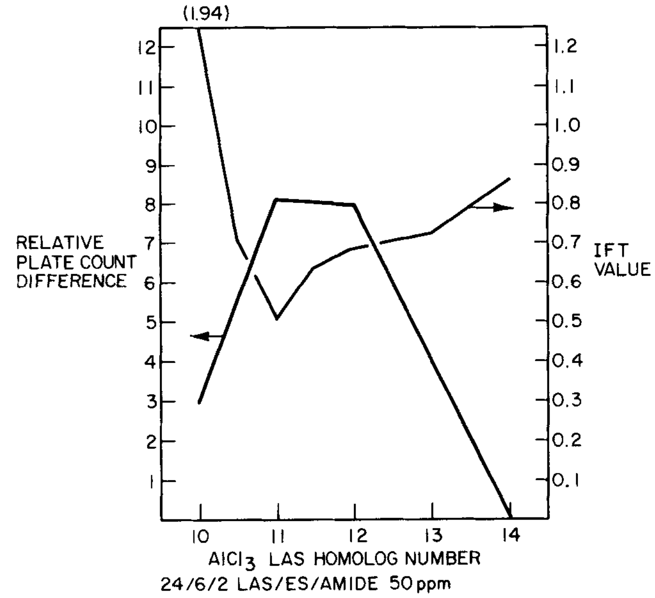

FIG. 5. Foam stability and interfacial tension of $AlCl_3$ LAS homologs at 50 ppm water hardness.

were then scaled to indicate their differences relative to the poorest performing homolog. In most cases the values were internally consistent enough to indicate the average plate count difference observed between any two homologs. This is only valid, however, for comparisons made within each separate graph where all five members of the homolog series were tested in simultaneous dishwashing test runs at the same set of experimental conditions. In all of Figures 1-13 a difference of ca. 1-2 plates represents a statistically significant difference.

Figure 1 indicates the performance of the $AlCl_3$ LAS homologs at 50 ppm. As indicated, the optimum homologs at 50 ppm are the C_{11} and C_{12} homologs, and the poorest is C_{14}. Figure 2 shows the corresponding chart for the HF homologs. Again, the C_{11} and C_{12} homologs are the optimum performers, and the poorest is the C_{14}. Figure 3 shows the performance of the $AlCl_3$ homologs at 150 ppm hardness. Now one sees a change in the shape of the curve, with the optimum moving over to C_{11} and the performance

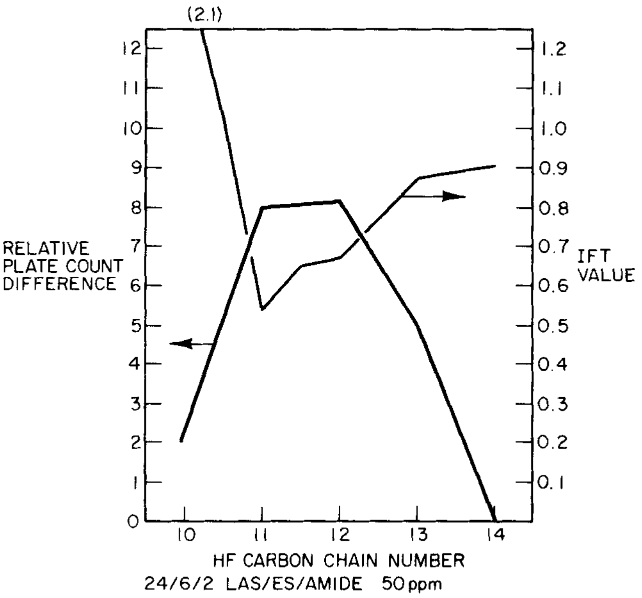

FIG. 6. **Foam stability and interfacial tension of HF LAS homologs at 50 ppm water hardness.**

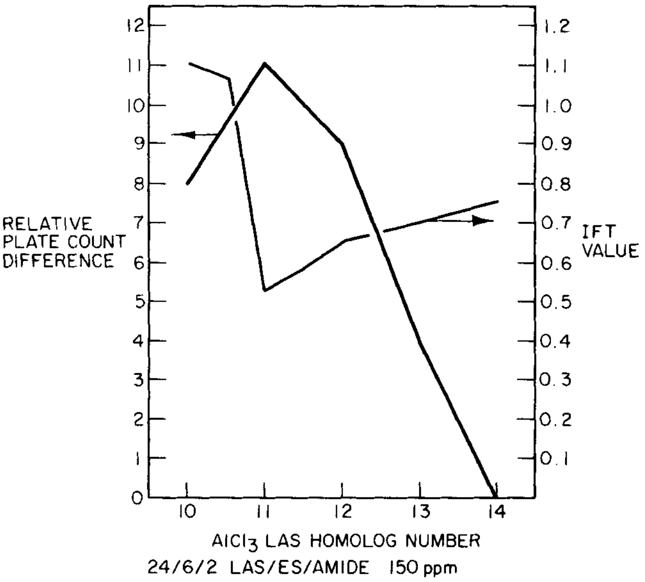

FIG. 7. **Foam stability and interfacial tension of AlCl$_3$ LAS homologs at 150 ppm water hardness.**

of C_{10} improving relative to C_{12} and C_{13}. In Figure 4, the performance of HF homologs also indicates that the performance has shifted over to C_{11}, and C_{10} has improved relative to the C_{13}.

Along with the dishwashing studies on these individual homologs, interfacial tensions (IFT) were run on the same formulations at the same experimental conditions, since a correlation between interfacial tension and the dishwashing test can be observed (5). These results are summarized in Figures 5-8, where the interfacial tension value curves are superimposed over the dishwashing performance curves. In Figure 5, with the AlCl$_3$ homologs at 50 ppm hardness, there is a minimum in the interfacial tension curve at the C_{11} homolog which corresponds roughly to the optiumum region of C_{11} and C_{12} for dishwashing performance. In Figure 6, with the HF homologs, again this minimum occurs in the region near C_{11} and, to some extent, C_{12} in the interfacial tension curve, and this corresponds roughly to the

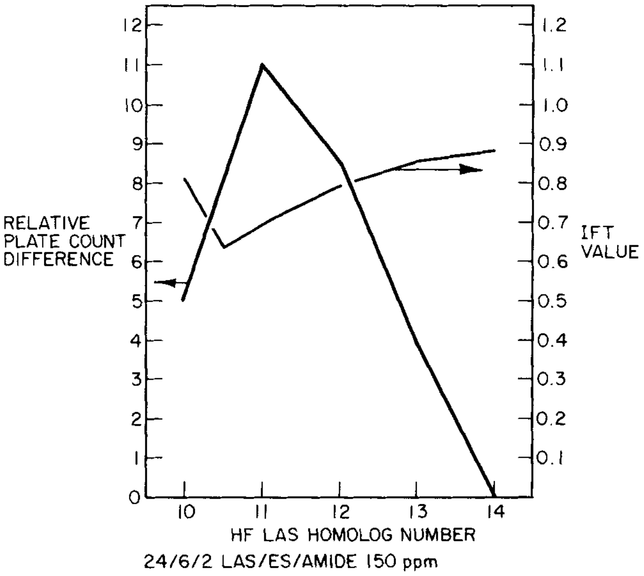

FIG. 8. **Foam stability and interfacial tension of HF LAS homologs at 150 ppm water hardness.**

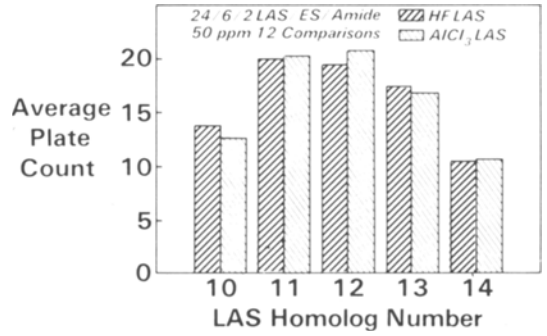

FIG. 9. **Foam stability comparisons of HF and AlCl$_3$ LAS homologs at 50 ppm water hardness.**

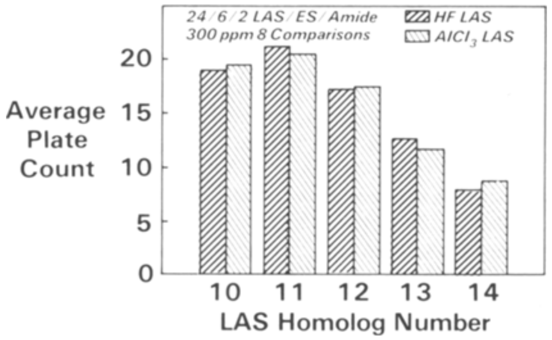

FIG. 10. **Foam stability comparisons of HF and AlCl$_3$ LAS homologs at 300 ppm water hardness.**

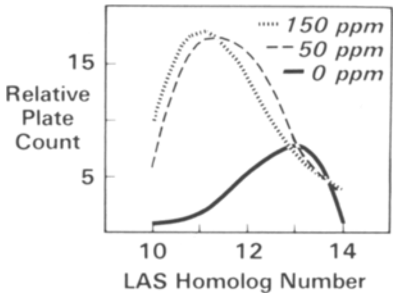

FIG. 11. **The effect of water hardness on the foam stability optimum (24% LAS/6% ES/2% amide).**

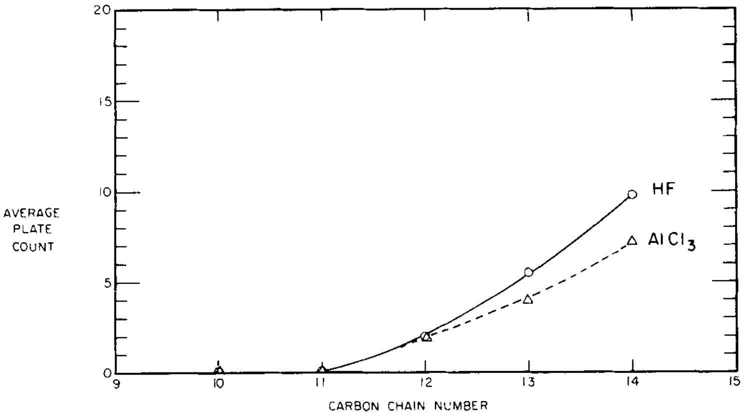

FIG. 12. Foam stability of HF and $AlCl_3$ LAS in a heavy-duty powder at 50 ppm water (77 F, concentration, 17% LAS/25% STPP).

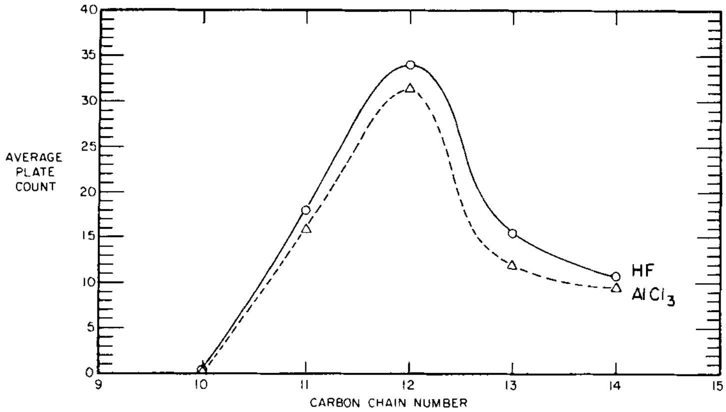

FIG. 13. Foam stability of HF and $AlCl_3$ LAS in a heavy-duty powder at 150 ppm water hardness (77 F, concentration, 17% LAS/25% STPP).

optimum in the dishwashing curve. In Figure 7, at 150 ppm for the $AlCl_3$ homologs, the interfacial tension curve superimposed over the dishwashing curve shows a correspondence between the optimum for dishwashing and the minimum for IFT. In Figure 8, the superposition of the curves indicates, again, a rough correspondence between the optimum for dishwashing performance and the minimum for interfacial tension.

Figure 9 summarizes the dishwashing performance at 50 ppm hardness for both the HF and the $AlCl_3$ homologs, with cross-comparisons made between homologs of identical carbon chain length of both the HF and $AlCl_3$ types. Here it is evident that the same trend of the C_{11} and C_{12} homologs being the optimum performers is indicated for both the HF and $AlCl_3$ types, and basically, there is very little difference between the two types of homologs at any particular carbon chain length. Much greater differences, however, are observed between homologs of different carbon chain lengths; for example, in going from C_{10} to C_{11}, both the $AlCl_3$ and the HF homologs increase in plate count about 5 plates. Figure 10 shows the comparisons between the HF and $AlCl_3$ homologs at 300 ppm hardness, and again, one sees the shift in the optimum at higher hardness level toward the shorter carbon chain lengths. Now the optimum has shifted over to the region of C_{10}-C_{11}-C_{12} carbon chain lengths. Again, there is very little difference between LAS homologs of the same carbon chain length with different phenyl isomer distributions. However, there is a much greater difference between LAS homologs of different chain lengths.

Figure 11 summarizes the dishwashing performance of the $AlCl_3$ LAS homologs at three different hardness levels. This is presented merely to illustrate the effect of increasing hardness on the foam stability. At 0 ppm hardness, the foam stability is very poor, and even the optimum homolog washes only about 6 or 7 plates. At 0 ppm hardness, the optimum LAS homolog is the C_{13}. When the hardness goes up to 50 ppm, the overall foam stability for all the LAS homologs increases. The optimum now is at C_{11} and C_{12}, and one sees that the total plate counts jump to ca. 20 plates. At 150 ppm, the optimum continues to shift to shorter carbon chain lengths, and the overall plate count remains about the same. This data is shown for the $AlCl_3$ homologs, and similar data is obtained for the HF homologs. This concurs with the results of this overall LDL foam stability study, which say there is no difference between the $AlCl_3$ and the HF homologs of the same chain length.

Foam Stability in Heavy-Duty Powders

The results of the studies on the foam stability of LAS homologs in a HDP formulation are illustrated in Figures 12 and 13. The values indicated are averaged total plate counts. The experimental conditions for these dishwashing tests were 77 F, 0.15% use concentration, and 50 and 150 ppm hardness on KEEN vegetable shortening. The formulation consisted of 17% LAS/25% STPP.

The data in Figures 12 and 13 indicate that foam stability is strongly dependent on hardness level. At a 0.15% use concentration, 25% STPP should sequester ca. 100 ppm hardness. Thus the dishwashing tests run below 100 ppm hardness are effectively at zero residual hardness, and the plate counts are low. At the 150 ppm hardness level, there is ca. 50 ppm residual hardness, and the plate counts increase dramatically.

At both high and low hardness levels, the foam stability is very dependent on carbon chain length. At low or zero residual hardness levels, the C_{10} and C_{11} homologs (both HF and $AlCl_3$ type) give no foam stability. As carbon chain length increases from C_{12} up to C_{14}, the foam stability increases for both HF and $AlCl_3$-type LAS. Above the zero residual hardness level, the optimum is very pronounced at C_{12} for both the HF and $AlCl_3$-type LAS.

The level of 2-phenyl isomer does have some effect on the foam stability of LAS in heavy-duty powders, as indicated in Figures 12 and 13. The HF (low 2-phenyl) LAS homologs show some foam performance advantage over the $AlCl_3$ (high 2-phenyl) LAS homologs. This foam advantage occurs at both low and high hardness levels, but at high hardness levels, the effect is overshadowed by the magnitude of the carbon chain length effect.

Measurements of the Gibbs surface excess absorption of both HF and $AlCl_3$ C_{13} and C_{14} LAS homologs at 0 ppm hardness show a difference between the two types of LAS. The HF LAS homologs had higher values (see Table II) for Gibbs surface excess absorption than the $AlCl_3$ homologs, indicating a greater concentration of surfactant monomers at the air/water interface. This may play a part in the foam stability difference between HF and $AlCl_3$ LAS in heavy-duty powders.

DETERGENCY

The results of the detergency study on the LAS homologs are indicated in Figures 14-21. Figure 14 shows the results of the LAS phosphate powder at 50 ppm hardness for both the $AlCl_3$ and the HF homologs plotted with the reflectance values as a function of the carbon chain length. On sebum soil at 50 ppm, the LAS homologs showed a slight detergency performance increase as carbon chain length increased. This occurred for both the HF and $AlCl_3$ type homologs. However, there is very little difference between the HF and the $AlCl_3$ homologs of the same carbon chain length. Figure 15 shows the detergency performance for the two types of homologs on sebum soil at 150 ppm hardness. Here the performance increase was greater, particularly on permanent press cloth, as carbon chain length increased. Again, there is very little difference between HF and the $AlCl_3$ homologs of the same carbon chain length. More dramatic, however, are the differences between LAS homologs of different carbon chain length.

Figure 16 shows the detergency performance for the $AlCl_3$ and the HF homologs on mineral oil soil at 50 ppm hardness. Here one sees a gradual increase in the detergency performance as carbon chain length increases, and again, there is very little difference between the HF and $AlCl_3$ homologs of the same carbon chain length. Figure 17 shows the performance on mineral oil at 150 ppm hardness. Here

TABLE II

Gibbs Surface Excess Adsorption Values for C_{13} and C_{14} LAS Homologs

	$\Gamma\ (mol \cdot cm^{-2})^a \times 10^{10}$
C_{13} $AlCl_3$	1.2
C_{13} HF	1.8
C_{14} $AlCl_3$	1.2
C_{14} HF	1.5

(J.A. Wingrave, private communication.)
[a] 0 ppm hardness, no STPP.

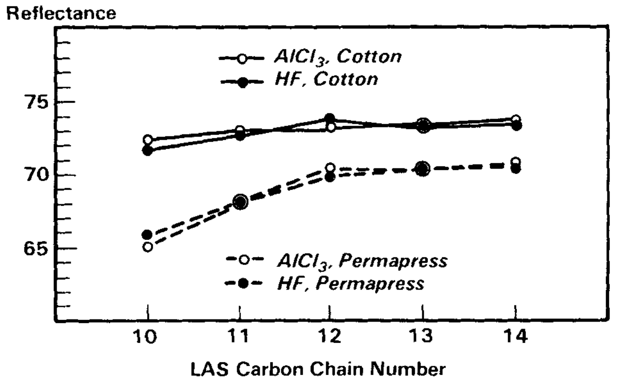

FIG. 14. Detergency of HF and $AlCl_3$ homologs on sebum at 50 ppm water hardness in a phosphate HDP (100 F, 0.15% concentration, 16% LAS/30% STPP/10% silicate).

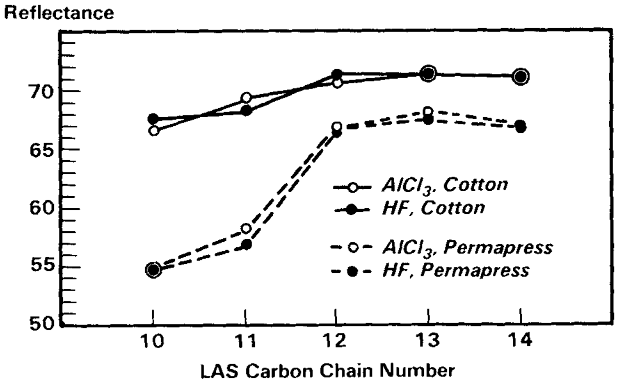

FIG. 15. Detergency of HF and $AlCl_3$ homologs on sebum at 150 ppm water hardness in a phosphate HDP (100 F, 0.15% concentration, 16% LAS/30% STPP/10% silicate).

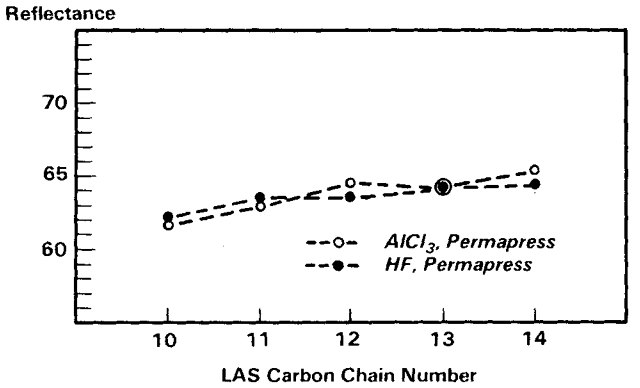

FIG. 16. Detergency of HF and $AlCl_3$ homologs on mineral oil at 50 ppm water hardness in a phosphate HDP (100 F, 0.15% concentration, 16% LAS/30% STPP/10% silicate).

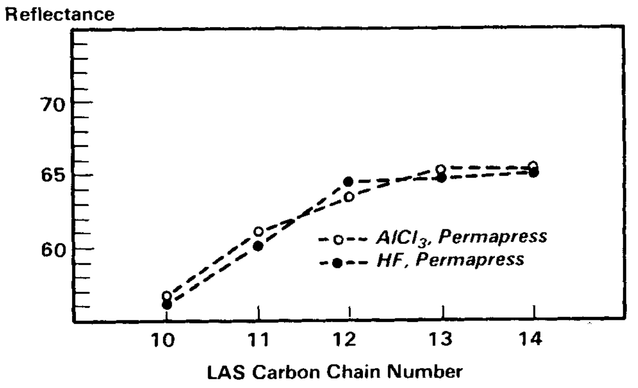

FIG. 17. Detergency of HF and $AlCl_3$ homologs on mineral oil at 150 ppm water hardness in a phosphate HDP (100 F, 0.15% concentration, 16% LAS/30% STPP/ silicate).

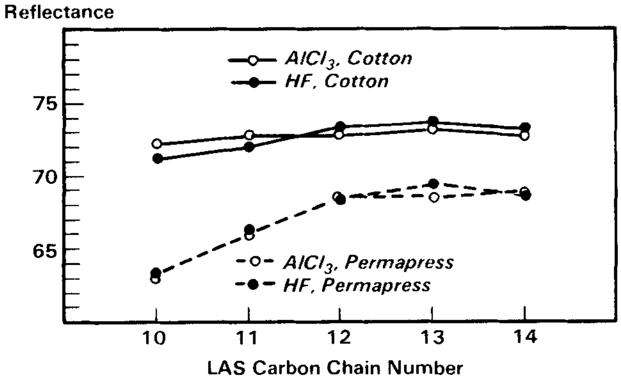

FIG. 18. Detergency of HF and $AlCl_3$ homologs on sebum at 50 ppm water hardness in a nonphosphate HDP (100 F, 0.15% concentration, 12% LAS/4% LMES/20% carbonate/20% silicate).

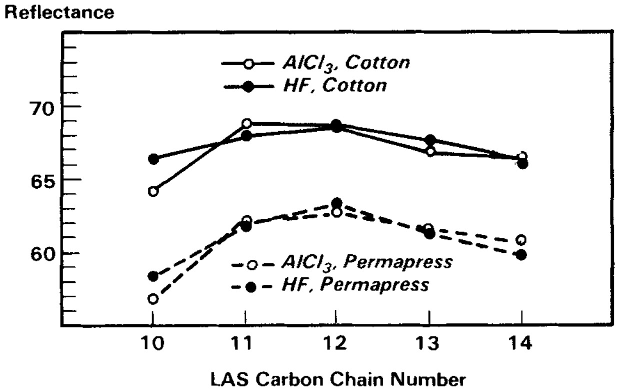

FIG. 19. Detergency of HF and $AlCl_3$ homologs on sebum at 150 ppm water hardness in a nonphosphate HDP (100 F, 0.15% concentration, 12% LAS/4% LMES/20% carbonate/20% silicate).

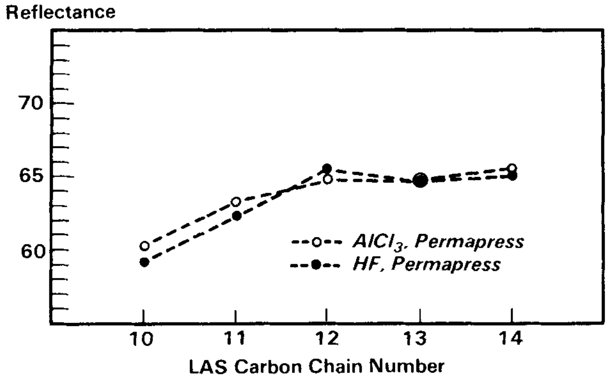

FIG. 20. Detergency of HF and $AlCl_3$ homologs on mineral oil at 50 ppm water hardness in a nonphosphate HDP (100 F, 0.15% concentration, 12% LAS/4% LMES/20% carbonate/20% silicate).

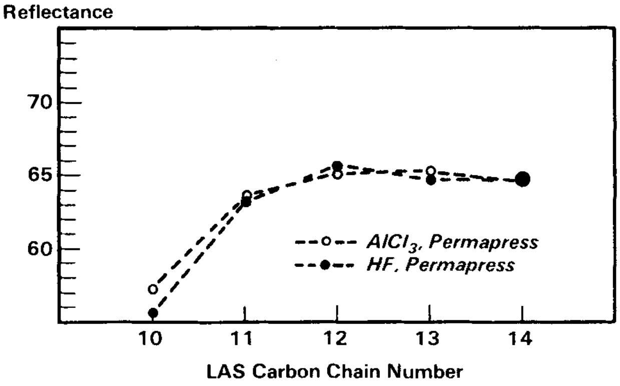

FIG. 21. Detergency of HF and $AlCl_3$ homologs on mineral oil at 150 ppm water hardness in a nonphosphate HDP (100 F, 0.15% concentration, 12% LAS/4% LMES/20% carbonate/20% silicate).

there is a greater trend in the increase in detergency performance as the carbon chain length increases, but still, there is very little difference between the HF homologs and the $AlCl_3$ homologs of the same carbon chain length. However, there is a rather large increase in detergency performance as carbon chain length for both the types of LAS changes from C_{10} to C_{12}.

Figures 18-21 shows the results of the homolog studies on the nonphosphate HDP containing LAS. The performance trends were generally similar to those in the phosphate HDP, except at 150 ppm hardness on sebum soil. Here the performance was indicative of an under-built system. The optimum for detergency was shifted towards the C_{11}-C_{12}-C_{13} range, with a slight performance decrease at C_{14} due to the detrimental effects of hardness.

In general, carbon chain length is the most important factor in determining foam stability and detergency performance. Differences in the performance among commercial types of LAS are primarily due to the carbon chain distribution. Phenyl isomer distribution, within current commercial limits of HF and $AlCl_3$ LAS, has little effect on the foam stability performance or interfacial tension of LAS in light-duty liquids and on the detergency performance of LAS in laundry products. Both HF and $AlCl_3$ LAS perform equally well and can be used interchangeably in high-performance products.

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