Recent Findings and Experiences with Alpha Olefin Sulfonates

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ABSTRACT

In the sulfonation and sulfation of alpha olefin (AO), linear alkylbenzene (LAB), and alcohol ethoxylate (AE), improved reaction yields and products' color were obtained by using the TO-Reactor recently developed in Lion Fat & Oil Co., Ltd., compared with those obtained in a conventional falling-film type reactor. These improvements especially were remarkable in the case of AO, so that light-colored alpha olefin sulfonate (AOS), having improved performance properties, was obtained without bleaching. For the performance tests, AOS was evaluated in several systems, together with some other surfactants, alcohol sulfate (AS), alcohol ethoxy sulfate (AES), linear alkylbenzene sulfonate (LAS), and alpha-sulfo fatty acid methyl ester (α-SEMe). AOS was one of the most useful surfactants for heavy duty powder detergents of low phosphate formulation because of its good detergency and foaming power, rinsing property, and free flowing property. Thus, bright white heavy duty powder detergents, containing 8% of P_2O_5, were developed with AOS (nonbleached), AES, LAS, sodium pyrophosphate (TSPP), and some other ingredients, which have been marketed in the household cleaning products field in Japan since 1976.

INTRODUCTION

Alpha olefin sulfonate (AOS) has been known since the 1930s (1), but only in the last decade has it been made on a commercial scale. At present, because of its performance properties (2), AOS has been used in household heavy duty detergents, light duty detergents, industrial cleaners, and in cosmetics. The consumption of AOS in these fields is expected to increase steadily in the future.

In view of eutrophication issues, a social demand for the development of detergents containing little or no phosphates has become evident. This paper is concerned with recent developments in the manufacturing process of AOS and in the formulation of heavy duty powder detergents of low phosphate-built type with AOS and other ingredients.

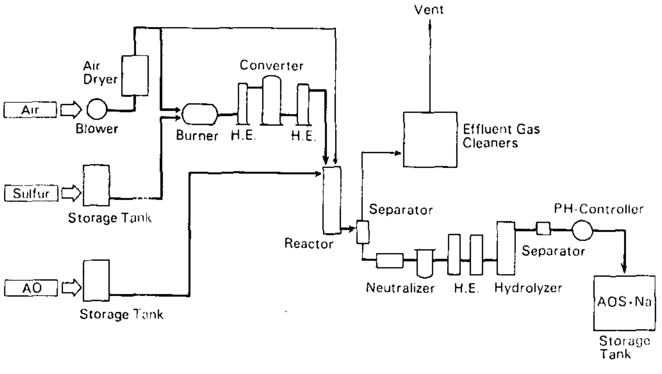

FIG. 1. Schematic flow diagram for SO_3 sulfonation of α-olefin.

OUTLINE OF MANUFACTURING PROCESS

Before describing the result of performance tests on AOS, it would be appropriate to touch briefly on our improved manufacturing process of AOS because making high quality AOS is of common interest to detergent industries around the world.

The manufacturing process of AOS consists of sulfonation of AO and hydrolysis of the sulfonated product as shown in Figure 1. In the reactor, AO is sulfonated with diluted SO_3 gas and, after separating the waste gas, the sulfonated product is mixed with sodium hydroxide solution in the neutralizer. The AOS is obtained by hydrolysis of the neutralized slurry, followed by pH-adjustment. To manufacture high quality AOS, it is necessary to take special care of the reaction and operating conditions in the sulfonation process. Therefore, particular methods are needed for controlling the reaction temperature and AO feed. These difficulties have been overcome by development of the TO-Reactor, a falling-film type reactor designed to make ideal "isothermal sulfonation" possible for manufacturing high quality products (3). To achieve "isothermal sulfonation," an inert gas stream, such as air, is supplied between the SO_3 gas and a film of the organic compound on the reactor wall so as to moderate the access of SO_3 gas to the film (4). Another technical advantage in the reactor is a special device that distributes an organic film of uniform thickness on the reactor wall. This is an important factor in achieving more uniformity of reaction and "isothermal sulfonation." Figure 2 shows a schematic

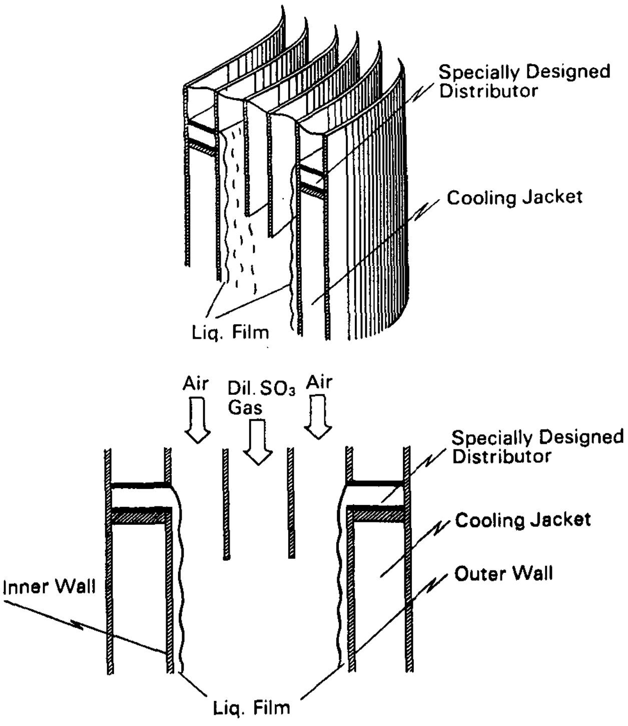

FIG. 2. Schematic diagram of reactor.

TABLE I

Comparison of TO-Reactor with Conventional Reactor

Surfactants	Reactor	Reaction yield, %	Klett color[b]	Di-sulfonate, %[c]
AOS-Na(C_{16}-C_{18})	TO	96.4	37	6
	Conventional[a]	93.1	154	11
AES-Na Dobanol-25 EO$\overline{P}$=3.0	TO	98.3	10	...
	Conventional[a]	98.0	18	...
LAS-Na	TO	98.7	12	...
	Conventional[a]	98.0	26	...

[a] Falling film reactor with high speed rotor.
[b] 5% Solution of active ingredient, nonbleached color.
[c] % Per active ingredient.

TABLE II

Sultone Contents[a] vs. Temperature

Temperature, C	Time, min	Sultone/active ingredient, ppm
140	20	568
140	60	327
165	20	200
170	20	80
180	20	30

[a] C_{16}-C_{18} AOS (AO mean mol wt 235). Sultone content max. present – all substances are included, which after alkaline hydrolysis form anionic surfactants, determined by two-phase titration.

diagram of the TO-Reactor. The results of sulfonation and sulfation of AO, linear alkylbenzene (LAB), and alcohol ethoxylate (AE) by the TO-Reactor are shown in Table I in comparison with the results by a conventional falling-film type reactor. As shown in the table, the effectiveness of the TO-Reactor in these reactions was apparent. Especially, the quality of AOS and reaction yield of AO were significantly improved. It was evident that the satisfactory result obtained with AOS was brought about by the achievement of the intended uniformity of reaction, despite the fact that it is difficult to control the reaction of AO with SO_3 in conventional falling-film type reactors, due to its extremely rapid, exothermal reaction.

The crude sulfonated product of AO consists of sultones and alkene-sulfonic acids, and their ratio is said to be 6:4 to 5:5 (5,6). Water-insoluble sultones are converted into water-soluble alkene sulfonate and hydroxy alkane sulfonate by a hydrolysis reaction with sodium hydroxide (7). The sultone is a relatively stable compound, though the stability mostly depends on the temperature. Therefore, severe hydrolysis conditions, such as higher temperature and longer time, are necessary to obtain AOS with low sultone contents, as shown in Table II.

EXPERIMENTAL PROCEDURE IN FORMULATION OF HEAVY DUTY DETERGENT

Surfactants

The following surfactants (sodium salts) were used for performance tests. Single carbon range AOS of C_{14}, C_{16}, and C_{18} were prepared from corresponding olefins which were obtained by fractional distillation of Ziegler olefins, by sulfonation with 5% excess SO_3 in a falling-film type reactor of laboratory scale. In the same manner, C_{14}-$_{18}$ AOS was also prepared from an olefin blend of the said C_{14}, C_{16}, and C_{18} AO.

In similar sulfonation conditions, LAS, AS, and AES were also prepared from LAB having C_{10} - C_{14} alkyl chain (mean mol wt 245), C_{12} - C_{15} oxo alcohol (Dobanol 25, Mitsubishi Petr. Chem. Co.), and alcohol ethoxylate of the said oxo alcohol (EO $\overline{p}$= 3.0), respectively. The α-SFMe was prepared from hydrogenated methyl tallowate by sulfonation with 20% excess of SO_3, followed by aging at 80 C for 1 hr in a lab-scale batch reactor. The prepared AOS and α-SFMe contained about 2% unreacted oils, but these were submitted to performance tests without de-oiling or any other refining.

Performance Methods

Detergency was measured by using a Terg-O-Tometer as well as with test swatches of 40-44% reflectance prepared by rubbing an artificial soil on the cotton cloths in the following washing conditions (8); liquor volume 900 ml, liquor ratio 1:30, temp. 25 C, and time 10 min. The washing liquors were prepared with the following composition: surfactant 0.021%, STPP 0.017%, alkaline builder 0.021%, and sodium sulfate 0.024%. Foamability was evaluated by measuring the foam height immediately after washing the shirts, soiled with artificial sebum oil, at 25 C (9). An electric washing machine with pulsator was used for this test. After the measurement of foamability, followed by rinsing twice, the rinsability (ease of rinsing) was evaluated from the foam left on the second rinsing liquor by visual observation according to nine rankings: +7, +6, +5, +4, +3, +2, +1, ± and –. In practical use, a ranking within – to +3 is necessary. The free flowing property of the formulated powder detergents was observed by measurement of an angle of repose on freshly spray-dried samples. A lower repose angle means better flowability in this test. For completely formulated powder detergents, it is desirable to have an angle below 40°.

These four performance tests were chosen for basic evaluation of the surfactants, taking into account the customary washing practices in Japan, as well as the practical considerations in manufacturing heavy duty powder detergents. Since Japanese housewives prefer high suds type detergents to the low suds types, foamability and rinsability are also important factors in the performance of detergents, together with detergency, in our country. Workability, in bulk storage and transportation of powder detergents, is an important factor in the manufacturing process and depends mainly on the free flowing properties of the powder. Decreasing the STPP content tends to have undesirable effects on the free flowing properties of the resulting powder detergents; flowability is, therefore, an important factor to be considered when formulating low phosphate-built powder detergents.

RESULTS AND DISCUSSION

Performance of AOS, LAS, AS, AES, and α-SFMe

Figures 3 and 4 show the effects of variations in the degree of water hardness upon the detergency and foamability of C_{14} - C_{18} AOS, LAS, AS, AES, and α-SFMe, in

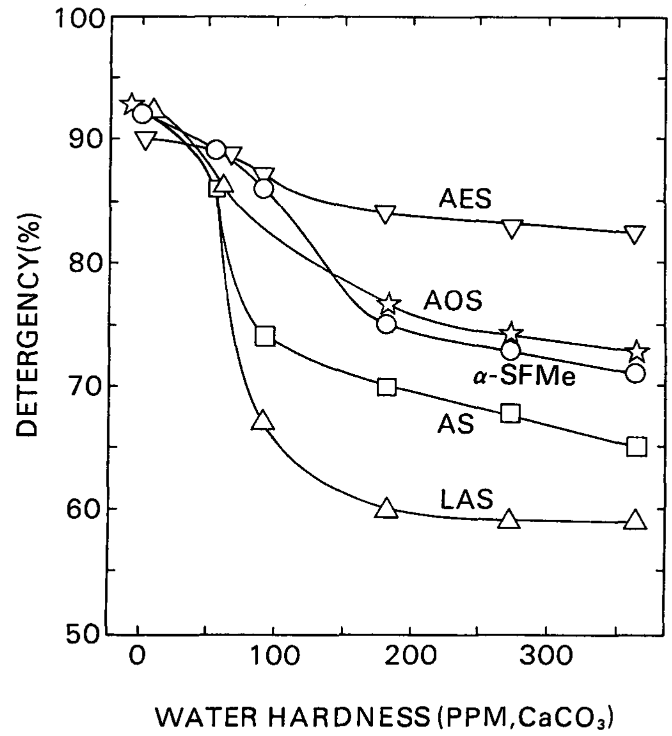

FIG. 3. Effect of water hardness of detergency of AOS, LAS, AS, AES, and α-SFMe in phosphate-built formulation. AOS: C_{14} - C_{18}, LAS: C_{10} - C_{14}, AS: C_{12} - C_{15}, AES: C_{12} - C_{15}, EO $\overline{p}$=3.0, α-SFMe: hydrogenated tallow fatty acid methyl ester.

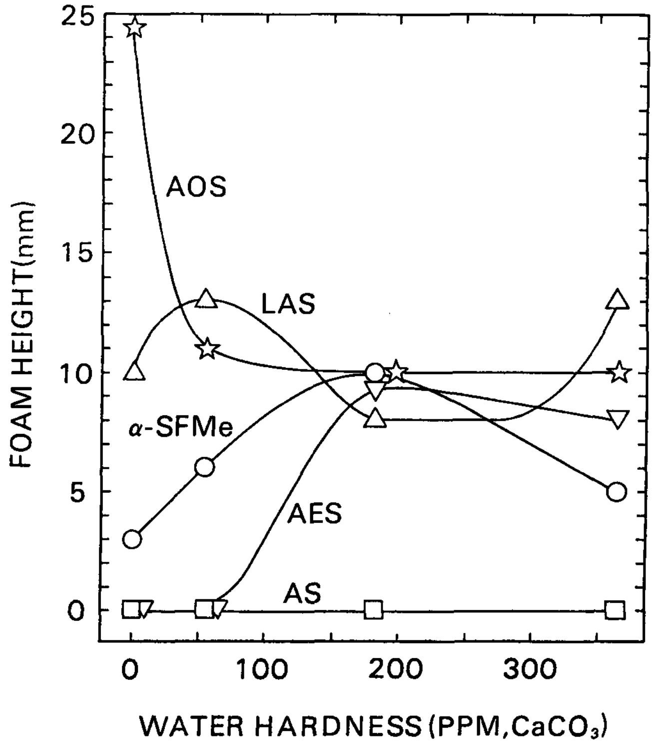

FIG. 4. Effect of water hardness on foam height of AOS, LAS, AS, AES, and α-SFMe in phosphate-built formulation.

phosphate-built formulations. In 0 and 54 ppm water hardnesses, all these surfactants showed sufficient detergency, whereas above 80 ppm water hardness, their detergency decreased with significant differences. In contrast to the results with AES, which indicates that the detergency is relatively insensitive to water hardness, the detergency of LAS and AS were severely affected with increased water hardness. The AOS and α-SFMe showed relatively good detergency. Thus the detergency was rated AES>$C_{14\text{-}18}$ AOS>α-SFMe>AS>LAS in 180-360 ppm water hardness. In the results of foamability, in relation to water hardness, rather complicated behaviors were observed, as illustrated in Figure 4. In 54-360 ppm water hardness the $C_{14\text{-}18}$ AOS showed relatively good foamability.

Carbon Number vs. Performance in AOS

To define further the effect of alkyl chain length in AOS on detergency and foamability, blends of C_{14}, C_{16}, and C_{18} AOS were evaluated in 54, 180, and 360 ppm water hardnesses. The results in phosphate-built formulations are shown in Figures 5 and 6. The detergency of C_{16} and C_{18} AOS declined considerably in 180 and 360 ppm water hardnesses. The detergency of C_{14} AOS was fairly insensitive to water hardness. Therefore, detergency in 54 ppm water hardness was rated C_{16}>C_{18}>C_{14}, but was in the order of C_{14}>C_{16}>C_{18} in 180 and 360 ppm water hardnesses. The foamabilities of C_{14} and C_{18} AOS were negligibly small in all three water hardnesses. An enhanced foamability was observed with C_{16} AOS in 180 and 136 ppm water hardnesses. Therefore, C_{14} AOS was recommended as an efficient surfactant for low suds detergents for the areas having high water hardnesses due to its good detergency and low suds property in high water hardness.

Influence of Di-sulfonate and Unreacted Oil in AOS

As shown in Figure 7, the detergency and foam height of $C_{14\text{-}18}$ AOS declined with increasing contents of di-sulfonate and unreacted oil. The foam height was extensively affected by these contents. Therefore, it could be said clearly that the development of the TO-Reactor has contributed improvement in performance of AOS because it provides high quality AOS having lower contents of un-

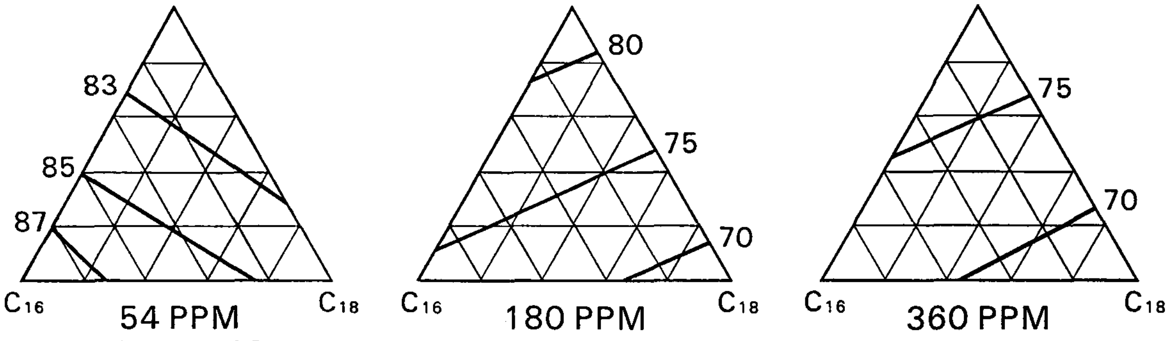

FIG. 5. Effect of water hardness on detergency of ternary system, C_{14} - C_{16} - C_{18}AOS, in phosphate-built formulation.

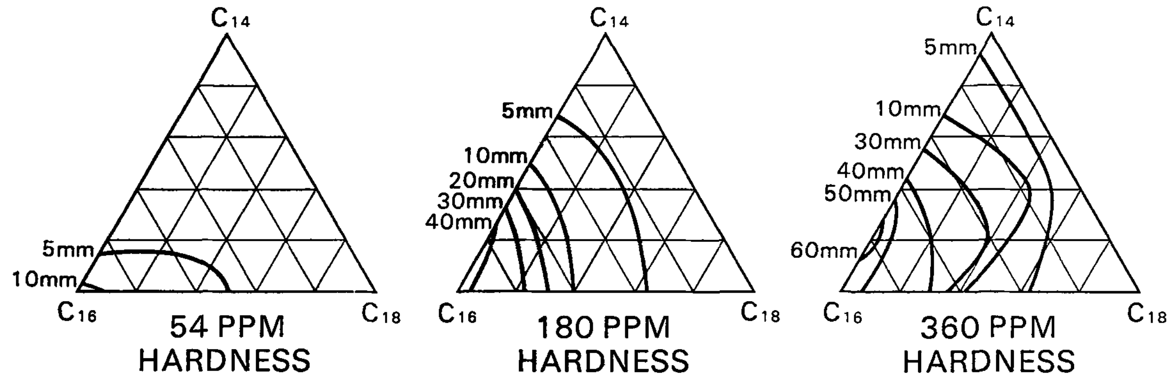

FIG. 6. Effect of water hardness on foam height of ternary system, C_{14}-C_{16}-C_{18} AOS, in phosphate-built formulation.

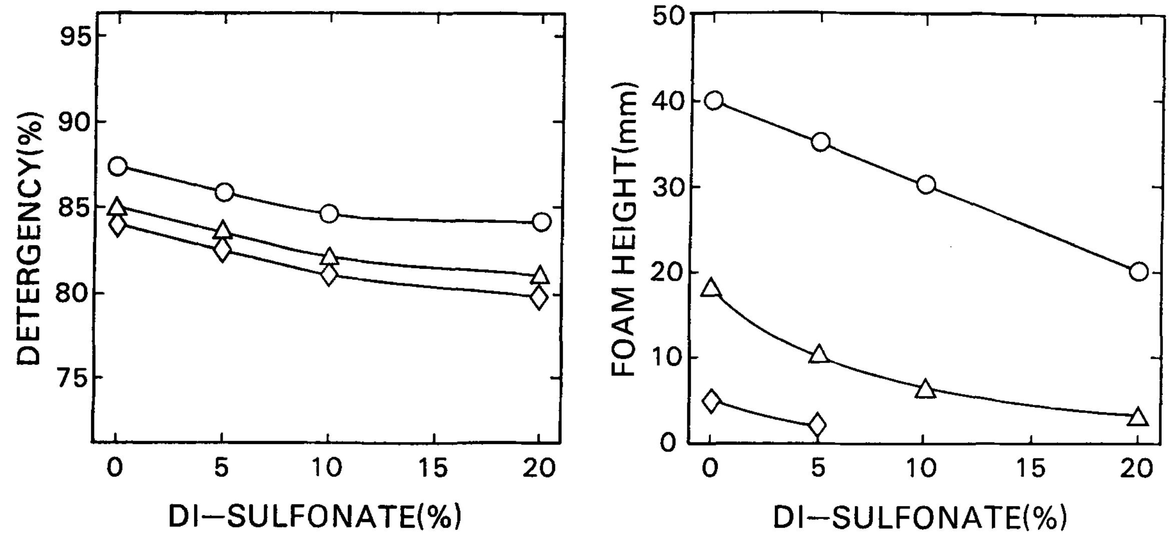

FIG. 7. Effect of di-sulfonate and unreacted oil on detergency and foam height in phosphate-built formulation. ○: unreacted oil/active ingredient = 0%; △: unreacted oil/active ingredient = 2%; ♦: unreacted oil/active ingredient = 5%.

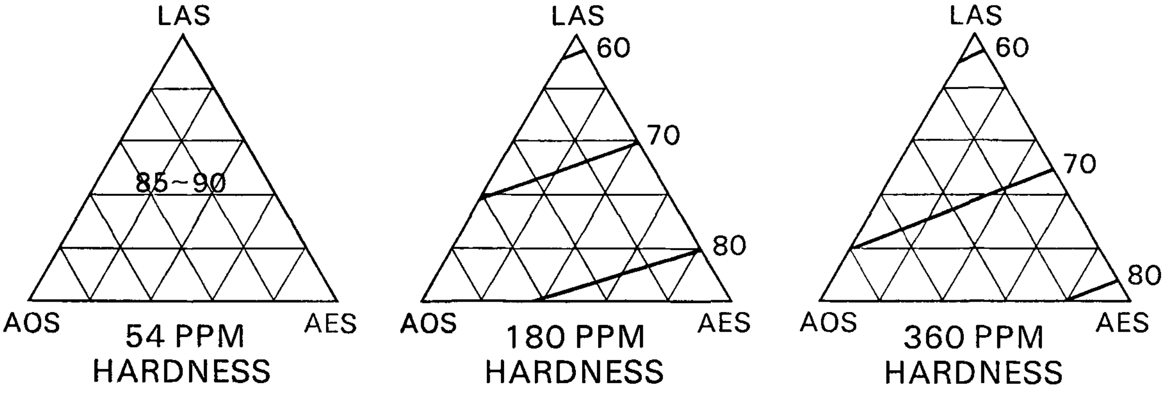

FIG. 8. Detergency of ternary system, AOS-LAS-AES, in phosphate-built formulation.

reacted oil and di-sulfonate, as shown in Table I.

Performance of AOS, LAS, AES Ternary System

In the detergency in 54 ppm water hardness, there were no significant differences among C_{14-18} AOS, LAS, and AES, but the detergencies in 180 and 360 ppm water hardnesses were in the order of AES > AOS > LAS as shown in Figure 8. Figures 9 and 10 show the foam height and the rinsability of C_{14-18} AOS-LAS-AES ternary system, respectively. In the foamability, a synergistic effect between AES and LAS was observed in 180 ppm water hardness. At all three water hardnesses, 54, 180, and 360 ppm, the rinsability of AES was poor compared with those of C_{14-18} AOS and LAS. For determination of flowability in C_{14-18} AOS, LAS, and AES ternary system, low phosphate-built powder detergents were prepared by using a bench-scale spray dryer. The phosphate content in the prepared detergents was 8% as P_2O_5. In this evaluation, AOS showed good flowability, whereas AES was poor in flowability (Fig. 11).

Development of Low Phosphate-built Powder Detergent with AOS

The STPP has been known as the most useful builder,

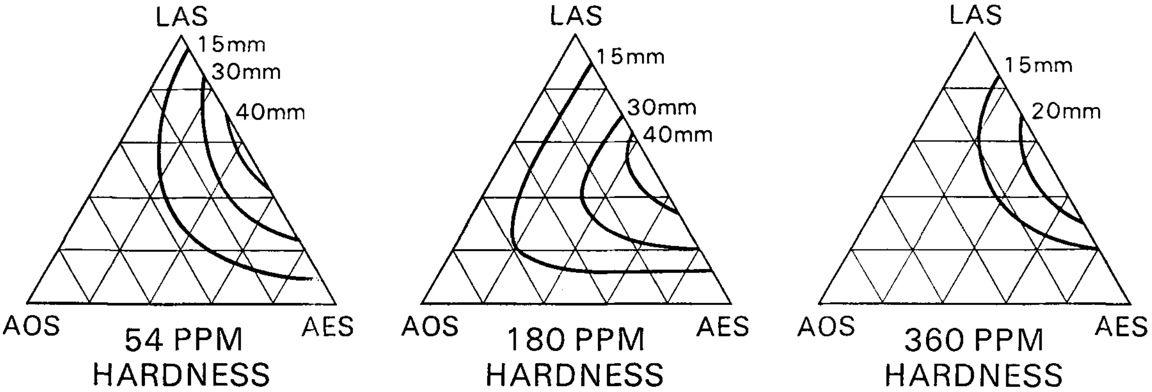

FIG. 9. Foam height of ternary system, AOS-LAS-AES, in phosphate-built formulation.

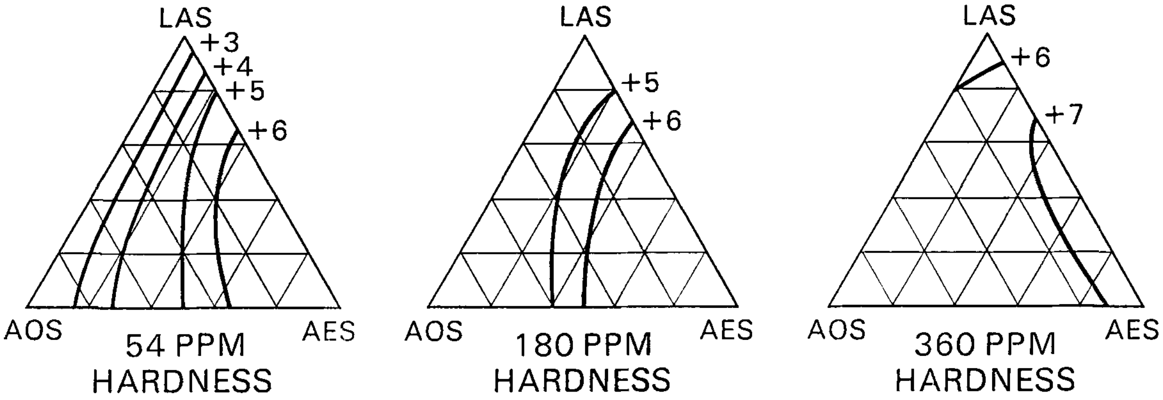

FIG. 10. Rinsability of ternary system, AOS-LAS-AES, in phosphate-built formulation.

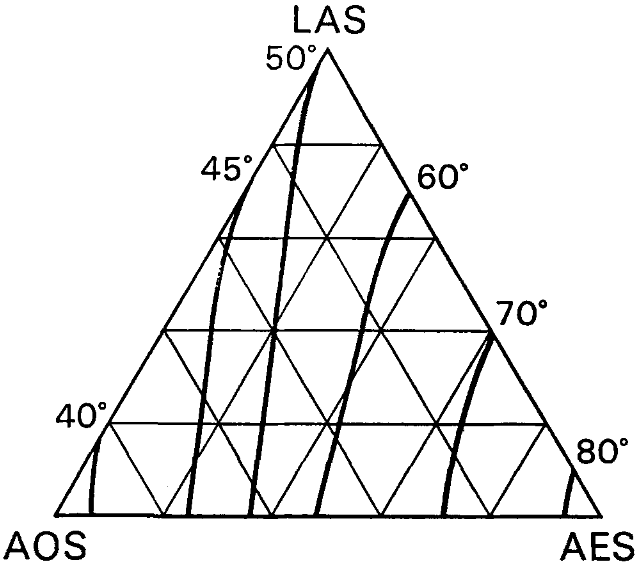

FIG. 11. Flowability of powder detergent of ternary system, AOS-LAS-AES, in phosphate-built formulation. Flowability expressed as angle of repose.

and used most widely in heavy duty detergents. However it was interesting to compare the builder effect of STPP and sodium pyrophosphate (TSPP) in a relatively low concentration range of phosphate. Figure 12 shows that TSPP was superior to STPP in phosphate contents below 12% as P_2O_5, in contrast to the results in the higher phosphate range. Along with discussions on eutrophication issues, there is a move to diminish phosphate content in heavy duty detergents in Japan, too. Generally, heavy duty powder detergents in Japan used to contain 15-20% of phosphate as P_2O_5 in the formulation, but at present the phosphate content has been controlled below 12% as P_2O_5. In order to decrease the phosphate content further, while retaining the detergency, there is a need for new technical development to be carried out in the fields of surfactant as

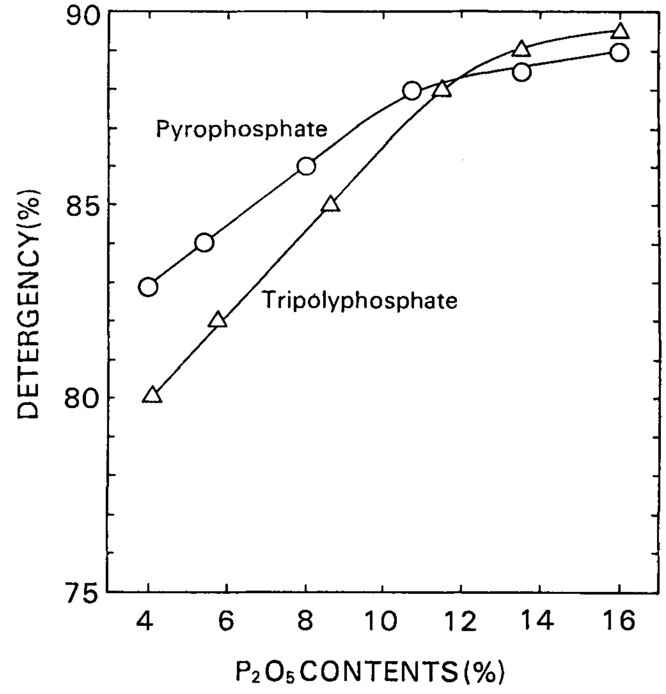

FIG. 12. Detergency v.s. P_2O_5 contents in phosphate-built detergent.

well as of formulation. Taking the most advantage of AOS technology, our company has marketed compact-type and regular-type powder detergents containing 12% of phosphate as P_2O_5, and, furthermore, developed modified powder detergents of the said two types containing only 8% of phosphate as P_2O_5 without any decline in the performance properties, by applying an advanced formulation technology. These have been marketed for some test sales since 1976.

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