Performance of Alpha Olefin Sulfonates Derived From Ziegler Olefins in Light Duty Liquid Detergents

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ABSTRACT

Single carbon number olefins derived from Ziegler technology were sulfonated in a continuous falling-film SO_3 reactor. The resulting alpha olefin sulfonate (AOS) was evaluated in a dishwashing test at several water hardnesses. Statistical analysis of the data led to the selection of compositions suitable for hand dishwash applications. AOS, prepared by sulfonating a blend of C_{14} and C_{16} olefins, was evaluated for hand dishwashing efficiency in a ternary mixture consisting of AOS, an alcohol ether sulfate and monoethanolamide. Regression equations calculated from the data permit the prediction of performance levels for all practical combinations of the three ingredients. The effect of unreacted olefin on AOS dishwash performance was also determined. With a binary blend of AOS and monoethanolamide it was shown that up to 5% free oil (based on AOS active) could be tolerated without significant deleterious effect.

INTRODUCTION

Alpha olefin sulfonate (AOS) has been known since the 1930's (1), but only in recent years has widespread commercial interest developed. Much of the reported work has centered on the technology of olefin sulfonation, reaction mechanisms and product composition (2-7). Published application data have mainly dealt with AOS from cracked wax olefins with emphasis on heavy duty laundry powder applications (8).

We have investigated the use of AOS from Ziegler olefins in light duty liquid detergents. Our objective was to determine (a) the relationship between AOS performance and olefin molecular weight, (b) the performance of AOS when substituted for LAS in a conventional LAS-alcohol-ether sulfate-monoethanolamide formula, and (c) the effect of AOS-free oil content on dishwash performance of formulated products.

EXPERIMENTAL PROCEDURES

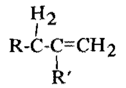
The Ziegler olefins used in this work are unique because of the manufacturing technique. A peaking process, whereby the normal Poisson-type carbon number distribution of the resulting olefins is narrowed, was employed. As a consequence of this processing method, the isomeric distribution of the olefins changes somewhat with molecular weight, depending upon the degree of peaking and carbon number peaked. The isomer distribution for a typical $C_{12\text{-}16}$ olefin cut, from one specific peaking and carbon number distribution process combination, is shown in Table I.

TABLE I

Composition of C_{12}, C_{14} C_{16} Olefins

Component, wt%	C_{12}	C_{14}	C_{16}	C_{14}/C_{16}
Carbon distribution by GLC				
C_{12}	99	1.3		0.4
C_{14}		98.0	3	66.2
C_{16}			96	33.4
Olefin type by NMR				
Vinyl	93.0	82.0	63.0	79.2
Vinylidene	3.7	10.9	27.2	12.5
Internal	3.3	7.1	9.8	8.3
Paraffin	0.3	0.3	0.4	0.3

As molecular weight increases, vinyl olefin content decreases, and vinylidene and internal olefin concentrations both increase. The vinylidene concentration increases at a significantly faster rate than the internal. Instrumental analysis of the vinylidene isomer indicates structure is



$$R\text{-}\overset{H_2}{\overset{|}{C}}\text{-}\underset{R'}{\underset{|}{C}}=CH_2$$

R' is predominantly an ethyl radical with lesser quantities of higher homologs. The internal olefins are a random distribution of the possible positions. Saturated hydrocarbon content is very low–typically 0.3% or less.

Single carbon C_{12}, C_{14} and C_{16} olefins were sulfonated in a bench scale falling-film SO_3 reactor using 4% excess SO_3. The sulfonic acids were worked up by refluxing 30 g in a known excess of 1 normal NaOH for 8 hr. Sufficient isopropanol and water were added to make a 5% solution of surfactant in a 1:1 isopropanol-water solution. Free oils were extracted with petroleum ether, and the alcohol was boiled off. Excess NaOH was back-titrated with 1 normal H_2SO_4 and the solution diluted to volume in a 500 cc volumetric flask. Sulfonation conditions were held constant, and as a result the unreacted oil content varied slightly between carbon numbers. To eliminated oil content as a performance factor, only de-oiled AOS was used in the study of performance vs. composition.

For formulation studies a 2:1 blend of C_{14} and C_{16} olefins was selected (Table I). The average molecular weight was 205, corresponding to a carbon chain length of 14.6. Total alpha content was 91+%, and the paraffin concentration 0.3%.

This olefin blend was sulfonated with 7.5% excess SO_3 to a free oil level of 2.3%. Saponification of the sulfonic acids was carried out in excess 1 normal NaOH at atmospheric pressure.

Klett color of the unbleached active (5% conc.) was 123 (40 mm cell length). The AOS was not de-oiled or bleached following the saponification. Neutralization of the excess NaOH with 1 normal H_2SO_4 to pH 8 was the only post treatment.

TABLE II

Verification of Response Surfaces[a]

A.

Component	Formula composition parts by weight	
Alpha olefin sulfonate (2:1 C_{14}-C_{16})	77	49
Lauric monoethanolamide	23	28
Alcohol ether sulfate	0	23

B.

Water hardness, ppm	Plates washed	
50	35	35
150	38	38
300	35	35

[a]Active concentration = 0.53 g/liter; water temperature = 49 C.

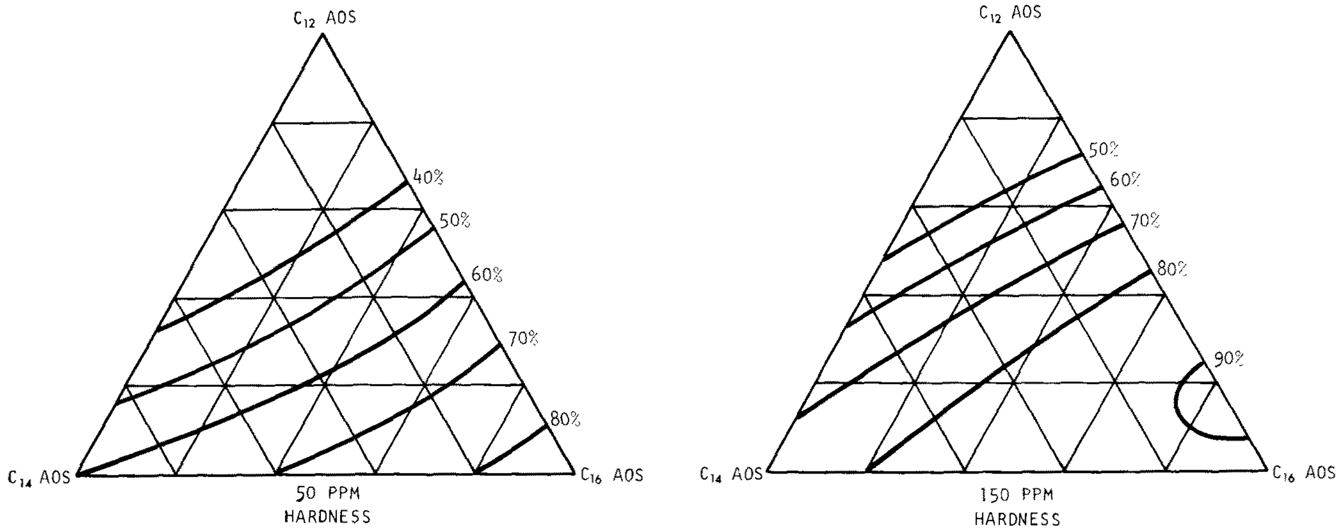


FIG. 1. Ternary carbon number vs. performance, unformulated (0.45 g alpha olefin sulfonate per liter). Miniature dishwashing test. Performance expressed as percentage of reference formulation. Water temperature = 49 C.

PERFORMANCE TESTING

The Miniature Dishwashing Test of Anstett and Schuk (9) was used for all performance testing. In this method a camel's hair brush is used to remove faintly dyed "Crisco" from watch glasses. Total active concentration was 0.45 g/liter; at this concentration an efficient surfactant system washed 25-28 plates in all but zero ppm water. A "dishwash reference formula" of 60 parts LAS, 30 parts alcohol ether sulfate and 10 parts lauric super diethanolamide was evaluated as part of each test sequence, and all performance values were expressed as a percentage of the reference. Regression equations were calculated from the performance values, and response surfaces plotted. Most data points were replicated four times or until the correlation coefficient between the observed values and the values calculated from the regression equation equaled 0.95 or better.

CARBON NUMBER VS. PERFORMANCE

Blends of de-oiled C_{12}, C_{14} and C_{16} AOS were evaluated in a ternary system using the Scheffé lactice design. The testing was in 50 and 150 ppm water and the AOS unformulated (Fig. 1). In both water hardnesses maximum dishwash performance was obtained with essentially 100% C_{16} AOS. In general C_{12} AOS acted to reduce performance, although in 150 ppm water an interaction between C_{12} and C_{16} AOS was noticed. The performance level was slightly higher, ca. 10%, in the harder water. This influence of water hardness on performance was apparent throughout the program.

To further define the effect of AOS molecular weight on dishwash performance, a ternary blend of C_{12},C_{14} and C_{16} AOS formulated 4:1 with lauric monoethanolamide was evaluated. Because the results in 150 ppm water substantiated those obtained with unformulated AOS, only one water hardness, 150 ppm, was investigated (Fig. 2). The response surfaces again indicated that maximum performance was obtained with 100% C_{16} AOS. However the

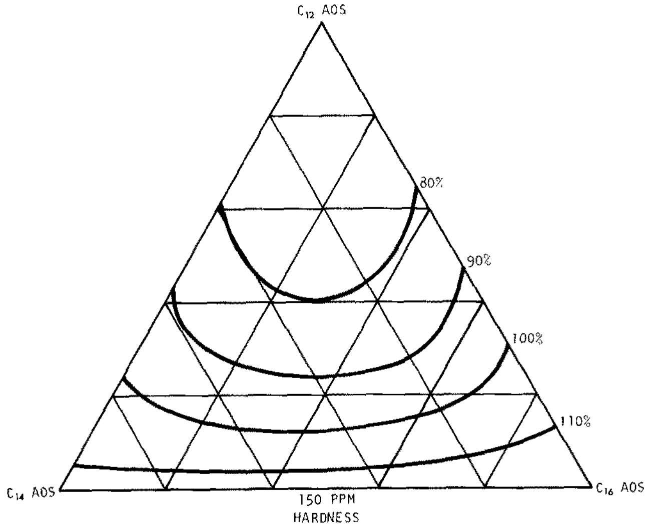


FIG. 2. Ternary carbon number vs. performance, formulated (0.36 g alpha olefin sulfonate per liter, 0.09 g lauric monoethanolamide per liter). Miniature dishwashing test. Performance expressed as percentage of reference formulation. Water temperature = 49 C.

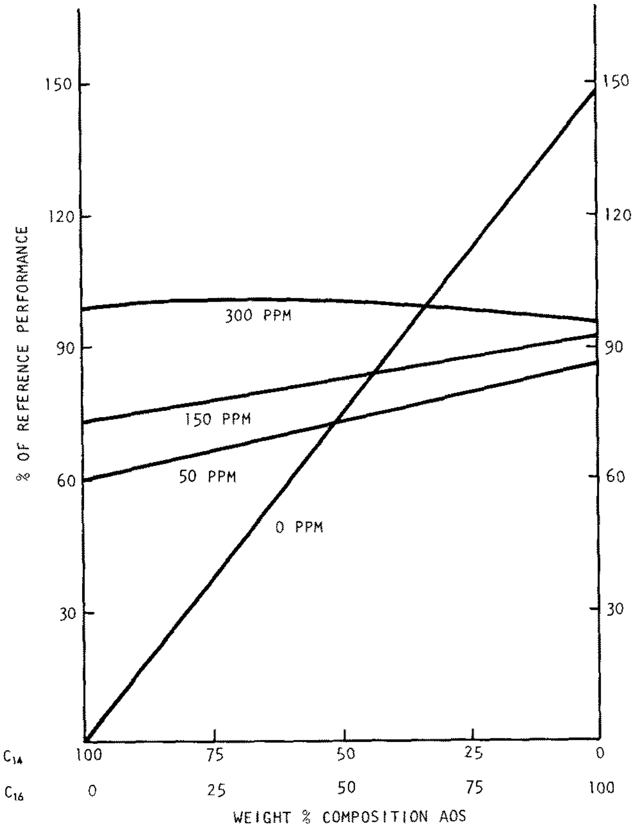


FIG. 3. Binary carbon number vs. performance, unformulated (0.45 g alpha olefin sulfonate per liter). Miniature dishwashing test. Water temperature = 49 C.

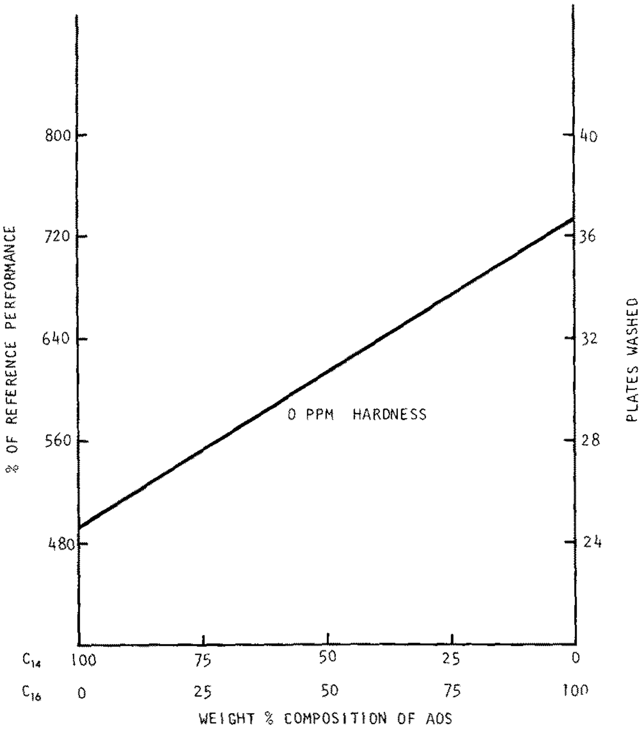


FIG. 4. Binary carbon number vs. performance, formulated (0.36 g alpha olefin sulfonate per liter, 0.09 g lauric monoethanolamide). Miniature dishwashing test. Water temperature = 49 C.

shapes of the response surfaces for the formulated system were somewhat different, compared to those obtained with unformulated AOS. The performance difference between C_{14} and C_{16} was much less in the formulated system, and the negative effect of C_{12} more pronounced. In the region of most practical interest, which we considered to be 3:1 to 1:3 of C_{14} and C_{16}, performance decreased essentially linearally with regard to C_{12} concentration increase. In addition the raw performance values disclosed that more plates were washed with blends of C_{14} and C_{16} AOS, rather than with pure C_{16} alone.

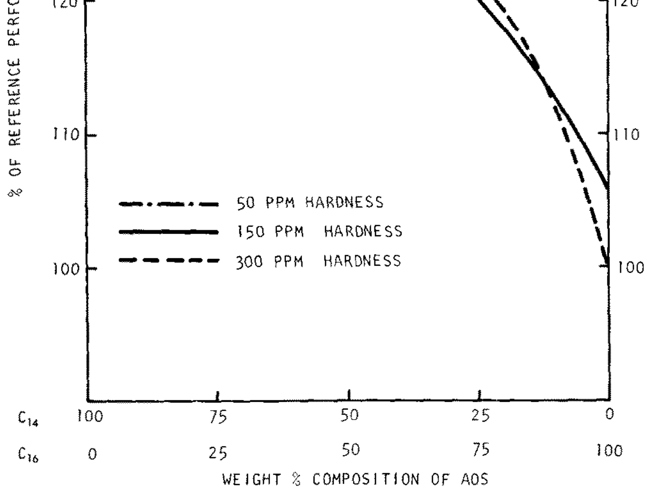


FIG. 5. Binary carbon number vs. performance, formulated (0.36 g alpha olefin sulfonate per liter, 0.09 g lauric monoethanolamide). Miniature dishwashing test. Water temperature = 49 C.

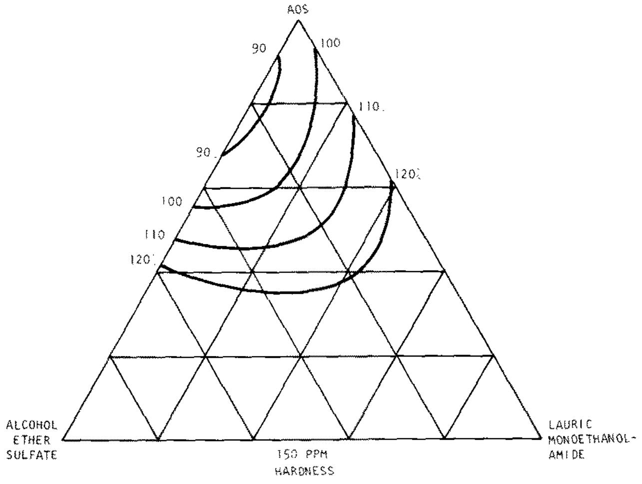


FIG. 6. Performance of ternary formulations of alpha olfin sulfonate, alcohol ether sulfate and lauric monoethanolamide. 2:1 C_{14}/C_{16} Olefin (mole wt = 205). Miniature dishwashing test. Performance expressed as percentage of reference formulation. 0.45 g active per liter. Water temperature = 49 C.

In as much as the preceding data from the three ternary systems were consistent in assessing the effect of C_{12} AOS on performance, and it appeared that maximum performance was achieved with mixtures of C_{14} and C_{16} we turned to evaluating binary blends of C_{14} and C_{16} AOS. The water hardness range was extended to include zero and 300 ppm, and the AOS tested, unformulated and formulated.

Response surfaces representing per cent of dishwash reference performance are shown as a function of unformulated C_{14} and C_{16} AOS composition in Figure 3. A definite effect on performance due to the test water hardness was evident. In zero ppm the effect was startling: C_{14} AOS washed no plates at all. Performance of C_{14} and C_{16} blends was linearily proportional to C_{16} content and increased by 15% for each 10% increment of C_{16}. A 33:67 mixture of C_{14} and C_{16} was equivalent to the dishwash reference formula. It should be brought out, however, that the dishwash reference performance was severely affected by the absence of hardness ions. The reference formula washed only 5-6 plates in de-ionized water vs. 25-28 in slightly harder water.

As water hardness increased, C_{14} AOS performance

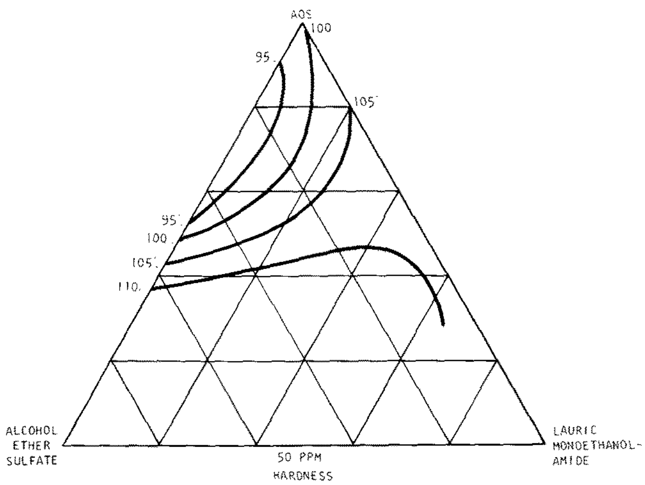


FIG. 7. Performance of ternary formulations of alpha olefin sulfonate, alcohol ether sulfate and lauric monoethanolamide. 2:1 C_{12}/C_{16} olefin (mol wt = 205). Miniature dishwashing test. Performance expressed as percentage of reference formulation. 0.45 g active per liter. Water temperature = 49 C.

TABLE III

Effect of Free Oil on AOS Performance[a]

Free oil in active, %	Plates washed: AOS containing free oil	Plates washed: AOS after de-oiling
7.5	29	34
5.2	31	31
4.5	32	31
3.5	29	30

[a]Alpha olefin sulfonate (AOS)(2:1C_{14}-C_{16}) = 0.36 g/liter; lauric monoethanolamide = 0.09 g/liter; water hardness = 150 ppm; water temperature = 49 C.

increased, until in 300 ppm it was equivalent to the reference. On the other hand C_{16} AOS was fairly insensitive to water hardness between 50-300 ppm. As a percentage of reference performance the C_{16} AOS washing ability continued to increase slightly with water hardness. However, when the small changes in reference performance between 50-300 ppm were considered, it was found the maximum number of plates were washed in 150 ppm water by unformulated C_{16} AOS.

The study of composition and performance was extended to formulated binary blends of C_{14} and C_{16} AOS. The hardness range again consisted of 0, 50, 150 and 300 ppm water. As mentioned above, the reference formula only washed 5-6 plates in zero ppm water. AOS formulated with lauric monoethanolamide washed many more plates under these same conditions. Consequently, because per cent of reference performance is less meaningful at this hardness, in Figure 5 the ordinate also identifies the actual number of plates washed. The slope of the response surface was nearly the same for the formulated system as for the unformulated case. Maximum performance was obtained with 100% C_{16} AOS, and the increase in performance was linear with respect to C_{16} concentration. The interesting contrast to the earlier data was the large increase in performance resulting from the amide addition. Formulated C_{14} AOS washed 25 plates, compared to none for 100% C_{14} AOS. A similar 25 plate increase was noted for the C_{16} AOS.

The performance of formulated C_{14} and C_{16} AOS in 50, 150 and 300 ppm water is shown in Figure 5. A significant effect on the performance curves resulted by replacing 20% of the AOS with amide. At 50 ppm despite many replications, no correlation of performance with molecular weight was achieved. All combinations were equivalent and ca. 25% better than the reference. This contrasts with the results obtained with unformulated AOS, where there was a definite advantage to C_{16} and the performance level ranged from 60-85% of the standard.

The effect of the amide on performance was greatest in 150 and 300 ppm water. At these hardnesses the slopes of the performance curves were reversed from those obtained unformulated. Maximum performance was obtained with pure C_{14} and was significantly superior to the standard. As C_{16} concentration increased the number of dishes washed decreased, until at 100% C_{16} the performance was only equivalent to the standard. The remarkable difference was in C_{14} performance with amide present. Unformulated performance in 150 ppm water was 26% less than the reference, while the performance of the formulated product was 37% greater. In 300 ppm water the synergistic effect of the amide was less than in 150 ppm, but the combination still produced a very significant 38% increase over unformulated AOS.

FORMULATION

In the study of performance vs. composition we observed very efficient dishwash performance for AOS in combination with lauric myristic monoethanolamide at a fixed 4:1 ratio. Consequently we desired to investigate AOS in conventional high performance light duty liquid formulations, most specifically as a replacement for LAS. A ternary system consisting of AOS, a linear C_{12-14} alcohol ethoxy sulfate, and lauric myristic monoethanolamide was selected for study. The AOS was derived from a 2:1 blend of C_{14}-C_{16} olefins and, as described earlier, was not de-oiled. Testing was at two water hardnesses, 50 and 150 ppm. Figure 6 shows the results at 150 ppm.

The response surfaces indicated a negative interaction between AOS and ether sulfate in the region of 70-90% AOS and 10-30% sulfate. Performance was ca. 5-10% less than that achieved with AOS alone. Performance increased with increasing amide concentration. Assuming AOS is the least expensive component and amide is the most expensive, for any desired performance level, maximum formulation cost is at the point of maximum curvature of the response surface. The 50 ppm evaluation results are shown in Figure 7. The response surfaces were similar to those for 150 ppm. The same negative interaction between AOS and ether sulfate in the absence of amide was evident. There was also a 5-10% lower performance level in the softer water in the region of higher amide concentrations. This is consistent with the results of the study of composition and performance where maximum performance was obtained in 150 ppm water.

The reliability of the response surfaces was checked by preparing two compositions which were expected to have equivalent performance in a given water hardness. One contained 23% amide and no ether sulfate, while the other contained 28% ether sulfate, 23% amide, and the balance AOS. The water hardness range was extended to include 300 ppm, and the active concentration was increased to 0.53 g/liter, slightly higher than that used before (Table II).

The results were as predicted by the response surfaces. At all three water hardnesses, the two formulas were equivalent. Again there were slightly more plates washed in 150 ppm water than in 50 or 300 ppm, as was evident in the carbon number and formulation studies.

An olefin blend of the 2:1 composition was sulfonated in a commercial falling-film SO_3 reactor. A 9% excess of SO_3 was used, and the resulting product after pressure hydrolysis contained 3.6% free oil based on the active. A 5% solution had a Klett color of 169, but a small amount of hypochlorite bleach reduced this to 46 Klett units. The bleached product was compared to laboratory prepared AOS of the same molecular weight in the Miniature Dishwashing Test at 50 and 150 ppm. The two materials were found to be equivalent within 95% confidence limits at both water hardnesses.

EFFECT OF FREE OIL ON DISHWASH PERFORMANCE

To ascertain the effect of free oil on dishwash performance, the C_{14-16} olefin blend was sulfonated with differing severity. A portion of the AOS was de-oiled, and comparative dishwashing tests were run. The AOS was formulated with monoethanolamide in a 4:1 ratio (Table III). With free oil levels of 3.5, 4.5 and 5.2%, there was no significant difference between oil-containing and de-oiled surfactants. The standard deviation of these six results was ± 1.0 plate, which in our experience is the precision of the dishwashing test. Only at the higher free oil level of 7.5% was a difference shown and performance decreased. This is in agreement with the investigation reported by Knaggs et al. (10), who found that free oil contents of up to 4% had little or not effect on Ross Miles foam or Draves wetting properties of AOS.

When the de-oiled AOS performance column is examined vertically, there appears to be a correlation between performance and original free oil content. As per cent free oil decreased, or conversely sulfonation severity increased, performance decreased. This correlation may be associated with the amount of disulfonate present or with the distribution of alkene and hydroxy sulfonate. We are currently investigating this aspect analytically in an attempt to further increase AOS dishwash performance.

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