The Workhorse Surfactants: LAS, Alcohol Sulfates, and Ether Sulfates

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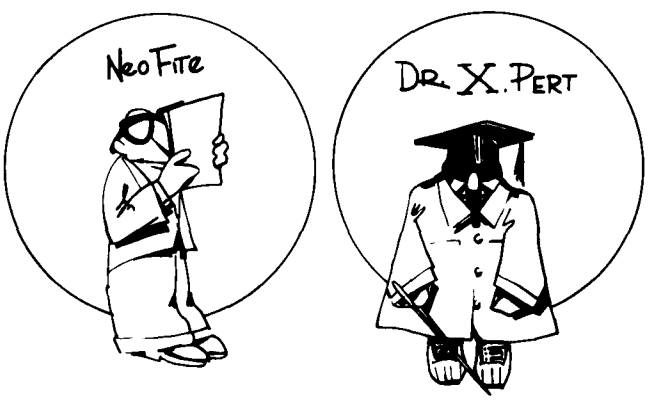
ABSTRACT

Relative market volumes are discussed illustrating why LAS, alcohol sulfates, alcohol ether sulfates, and branched chain alkylene benzene sulfonates are called "workhorse" surfactants. Typical heavy duty powder, heavy duty liquid, and light duty liquid formulations from around the world are given for each material. Low mole ether sulfates for heavy duty powders are discussed as to chemical constituency and performance. Comparisions of LAS to paraffin sulfonates and olefin sulfonates are given for light duty liquid formulations. Shampoo performance advantages of alcohol sulfates over olefin sulfates are illustrated.

INTRODUCTION

Since there are very few panel discussions or departures from the normal types of papers and since this is a review paper on well-known surfactants, it will take the form of an interview. The interviewer, Mr. Neo Fite, has solicited from attendees several questions that he will ask Dr. X. Pert, who is a surfactant chemist of some 30 year's experience. With that introduction, the first question please, Mr. Fite.



Fite: Why these products? They have all been well known for some time, even by us less experienced chemists.

Pert: One of the purposes of this conference is "to share and discuss the practical technology of soaps and detergents," and these products: LAS ether sulfate, alcohol sulfate, and hard alkylbenzene sulfonate along with the nonionics that Mr. McKenzie will discuss are the major products used in household detergents today. Therefore, in a conference of this type, these products should be reviewed.

Fite: What are the relative volumes of these products compared to some of the "newer" materials such as SAS and AOS?

Pert: Table I shows the extremely large volumes of alkylbenzene sulfonate, both hard and soft. These materials had a consumption in 1976 of almost four times that of all the other products (Table II). The alcohol sulfate totals shown in Table III at 82,000 metric tons are considerably lower than for both SAS and AOS combined. So, you see why these top four are called "workhorse" surfactants.

Fite: What types of formulations utilize LAS?

Pert: All types. Heavy duty powders, heavy duty liquids, light duty dishwashing liquids, light duty powders, household cleaners, industrial detergents – all types.

Fite: Can you give me some examples?

Pert: The largest volume usage of household formulations is naturally in heavy duty powders. The first type of formulation utilizes 15 to 20% active LAS and is predominantly in the U.S., Japan, most of Europe, and in Australia.

The second type, which uses 20 to 30% LAS, is found in Southern Europe, South America, and many other countries. Many places also use this formulation substituting hard alkylate for the soft linear alkylate.

Formulation No. 3 is a mixed active formulation containing 7 to 10% LAS and 10 to 14% ether sulfate. The largest selling product in the U.S. would fit into this category.

The fourth type of formulation is another mixed active formulation, but it contains a mixture of 10 to 14% LAS and 1 to 6% nonionics.

In light duty liquid formulations, LAS is widely used in conjunction with alcohol ether sulfates in formulations containing 14 to 20% LAS and 4 to 10% ether sulfate. These formulations are especially prevalent in the U.S., Japan, and Europe.

A second type of formulation utilizes LAS as the only active ingredient and would usually contain 15 to 25% LAS.

A third type of formulation consisting of 14 to 17% LAS and 16 to 21% ether sulfate contains a higher ratio of ether sulfate to LAS than those mentioned before. Although optimum foam stability can be gained in formulations containing a higher LAS/ES ratio, this particular formulation is used in one of the top three products in the

TABLE I

1976 Surfactant Consumption

	Sulfonate (1,000 metric tons)	
	Hard ABS	Soft LAS
Asia & Oceania	160	135
Western Europe		500
U.S.		360
South America	255	20
U.S.S.R.	---	---
	415	1,015

TABLE II

1976 Surfactant Consumption

	Ether sulfate	Alcohol sulfate	SAS	AOS
U.S.	150	36	---	5
Western Europe	70	40	50	5
Japan	20	6	tr	tr
	240	82	50	10

TABLE III

1976 Surfactant Consumption

	Totals (1,000 metric tons)
Hard ABS	415
Soft LAS	1,015
Ether sulfate	240
Alcohol sulfate	82
SAS	50
AOS	10

U.S. and satisfies other marketing needs than foam stability alone.

Heavy duty liquids have gained little marketing interest outside of the U.S. and Japan. A major product in the U.S. is a built heavy duty liquid which contains about 10% LAS along with tetrapotassium pyrophosphate.

A second built formulation is used where phosphate has been outlawed. In this formulation, citrate replaces the TKPP, and higher amounts of LAS are used along with an alcohol nonionic, e.g., 14 to 17% LAS with 4 to 7% nonionic with citrate.

Nonbuilt heavy duty liquids will contain from 10 to 18% LAS and 30 to 40% alcohol nonionic. The LAS is generally the sodium salt, but in at least one major product, the triethanolamine salt is used.

In Japan, both primary and secondary alcohol ether sulfates have been used in the anionic portion of the formulation.

Fite: Which molecular weight LAS is used for the different types of products?

Pert: In general, the lower molecular weight alkylate, approximately 238, is used in liquid applications and the higher molecular weights, from 244-262 (C_{12}-C_{13}), are used in powdered products. Figure 1 illustrates the detergency of a phosphate-built laundry product vs. alkyl chain length.

These curves show that at both hardness levels studied detergency increases with increased molecular weight. There can be different conclusions with different hardnesses, with different builders, and with mixed active systems. Generally, however, alkylates of 244 may perform as well as higher molecular weights under some conditions of hardness, builder type, and mixed active systems, but seldom will the 238 molecular weight alkylate perform as well in detergency.

Fite: Why is so much LAS used in comparison to other anionics such as SAS and AOS?

Pert: *Versatility* is one factor. LAS is used in almost all types of household products. The major applications for SAS and AOS are in liquids because of improved solubilities. In powders there are no advantages for SAS and AOS, and spray-drying properties are "different."

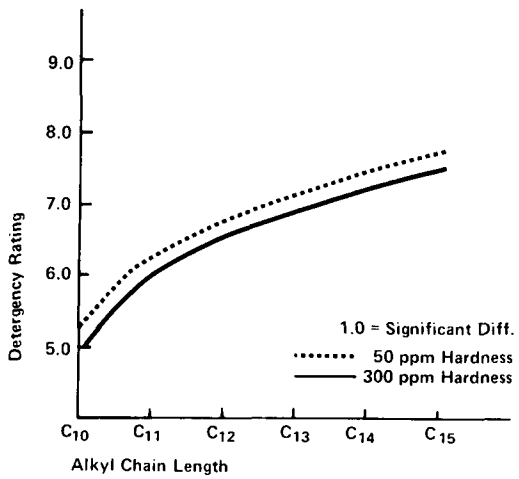


FIG. 1. Effect of alkyl chain length on heavy duty detergency.

As far as *performance* in liquids is concerned, the data in Table IV show a comparison of three anionic materials in light duty liquid foam stability.

From these data you can see that LAS and SAS performed marginally better than AOS at low hardness levels and all are approximately the same at high hardness. The choice of product then will be determined primarily by economics. The solubility of SAS may make its use feasible on a cost/performance basis in some liquid formulations.

LAS has a long history of use with an unquestioned *safety* record.

Availability has to enter into the choice of product since large quantities of SAS are only available in Western Europe, and AOS is available in the U.S. and Europe. Even in these cases both SAS and AOS are normally offered in aqueous solutions of 40 to 60% active and, therefore, transportation costs and handling have to be considered.

Fite: What are the properties that make ether sulfate a major product?

Pert: *High foaming* is characteristic of ether sulfate especially in conjunction with LAS. A synergism exists when LAS and ether sulfate are used together in that higher foam stability is obtained than with either ingredient alone. Ether sulfates have *excellent solubilities* and are, therefore, widely utilized in liquid formulations.

Ether sulfates have *good hard water tolerance* which becomes an important factor in areas where phosphate usage must be limited by legislation.

Fite: Could you give me some examples of formulations where ether sulfates are used?

Pert: Light duty liquids, shampoos, and currently in mixed active formulations of laundry powders, especially where legislation has forced a phosphate limitation.

TABLE IV

Foam Stability Comparisons

Sulfonate[a] type	Plates washed at 115 F, 0.1% conc.	
	50 ppm	300 ppm
LAS	25	23
AOS	23	23
SAS	25	22

[a]25% sulfonate, 2% alcohol ether sulfate, 2% lauric-myristic monoethanolamide.

$$ROH + H_2C\text{-}CH_2 \longrightarrow RO(CCO)_{1.5}H$$

Low-Mole Ethoxylate

$$RO(CCO)_{1.5}H + SO \xrightarrow{2)NaOH} RO(CCO)_{1.5}SO_3Na$$

Low-Mole Ether Sulfate

$$ROH \xrightarrow[(2)\ NaOH]{(1)\ SO_3} ROSO_3Na$$

$$RO(CCO)_3H + SO_3 \xrightarrow{2)NaOH} RO(CCO)_3SO_3Na$$

Typical Ether Sulfate

FIG. 2. Low-mole ether sulfate.

Fite: Are the light duty liquid formulations the same ones you mentioned before?

Pert: Yes, with one addition. We talked about types 1 (14 to 20% LAS plus 4 to 10% ether sulfate) and 2 (14 to 17% LAS plus 16 to 21% ether sulfate). In type 2, ether sulfates were formerly used with AOS in the U.S. In mid-year 1976, the AOS was replaced by LAS and now no major products in the U.S. contain AOS.

The third formulation type is an all ether sulfate active. I say all ether sulfate (20 to 30%), but this type of formulation usually contains a small amount of amine oxide and sometimes alkylglyceryl ether sulfonate. Three major products in the U.S. have this formulation.

Fite: You said ether sulfates are also in heavy duty powders?

Pert: Yes. This type of formulation (7 to 10% LAS and 10 to 14% ether sulfate) started out with the ether sulfate used as a replacement for alcohol sulfate in phosphate legislated areas. Now the ether sulfate is found in phosphate formulations as well.

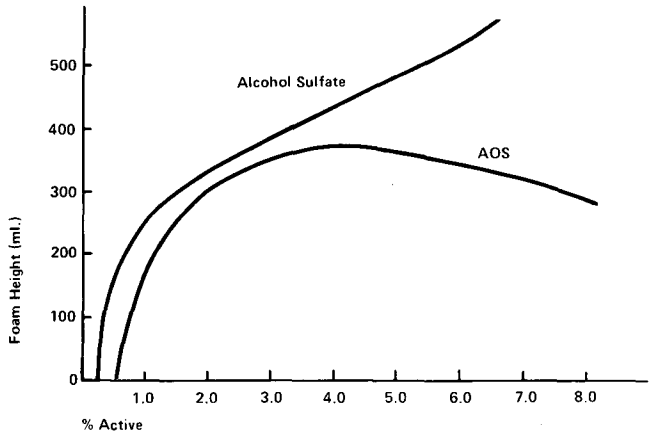


FIG. 3. Foam height @ 50 ppm hardness sodium alcohol sulfate vs. AOS.

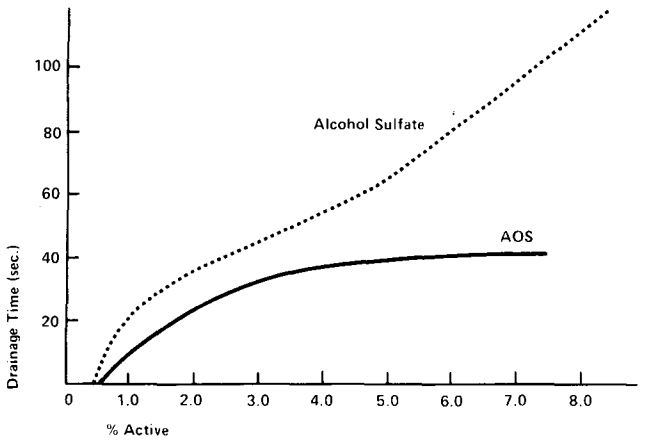


FIG. 4. Drainage time @ 50 ppm hardness sodium alcohol sulfate vs. AOS.

Fite: Is this the same ether sulfate used in dishwashing?

Pert: I prefer to call the ether sulfate currently used in this application a low-mole ether sulfate (LMES). That is, an alcohol ethoxylated to only 1½ moles EO and then sulfated.

At the top of Figure 2 is the reaction for a typical 1½ mole EO ether sulfate. First the ethoxylation, then sulfation, and neutralization. In the ethoxylation step there is a considerable amount of unethoxylated alcohol which in turn would sulfate making the LMES actually a blend of alcohol sulfate and ether sulfate.

Detergency tests have shown that similar results can be obtained by (a) blending alcohol with three mole or higher ethoxylate followed by sul-

TABLE V

Terg-O-Tometer Tests

Builder	Detergency[a]			
	10% LAS/5% LMES		15% LAS	
	Hardness (ppm)		Hardness (ppm)	
	120	180	120	180
25% STPP	71.9	67.2	71.8	66.1
15% STPP	67.6	64.5	66.8	60.4
25% Na_2CO_3	66.6	67.1	65.0	65.5
50% Na_2CO_3	71.4	71.2	70.8	70.0
15% Silicate, 8% $NaBO_3$	62.4	61.3	58.7	57.6

[a]Reflectance (R_d), sebum soil, permanent press, 120 F.

fation or (b) ethoxylating an alcohol to 1 or 1½ moles EO followed by sulfation. Therefore, what I call an LAS and LMES formulation is sometimes referred to as a ternary system of LAS, ether sulfate, and alcohol sulfate.

Fite: Does that low-mole ether sulfate really work?

Pert: Results of Terg-O-Tometer detergency at 120 F, 0.15% concentration, with sebum soil on permanent press (65/35, cotton/dacron) cloth at both 120 and 180 ppm hardness are shown in Table V. A difference of 1.0 in reflectance is necessary to be significant at a 95% confidence level.

At 120 ppm there are no differences in detergency between an LAS formulation and an LAS/LMES formulation at 25% tripolyphosphate. There is a marginal difference with 15% STPP and a significant difference in foam of LMES with all of the poorer builder systems.

At 180 ppm the hardness resistance of the LMES is even more evident with significant differences in favor of the LAS/LMES blend with all builders.

Fite: Since time is growing short, where are alcohol sulfates used?

Pert: In shampoos, cosmetics, toothpaste, laundry products. In the laundry application, alcohol sulfates were widely used in both Europe and the U.S., but that usage has dropped considerably lately. In the U.S. the LMES has partially replaced the alcohol sulfate as I mentioned earlier.

The largest usage is in shampoos. Some of these contain 20 to 30% active along with an alkanolamide or amine oxide as a foam stabilizer.

Fite: How do alcohol sulfates compare with AOS in shampoos?

Pert: Though foam of AOS compares favorably with alcohol sulfate at extremely low concentrations, at the actual shampoo use concentrations alcohol sulfates give the thick, copious, long lasting foam needed for quality shampoos.

The chart of foam height in Figure 3 shows that at the normal shampoo concentrations, above 3%, alcohol sulfates are superior to AOS. The need for higher use concentrations are due to heavy soil loads as Figure 4 indicates.

Foam stability, as indicated by a film drainage time, shows similar advantage for alcohol sulfate.

Fite: What are your prognostications for the future for LAS, alcohol sulfates, and ether sulfates?

Pert: As phosphate usage is legislated, higher active contents of all types of surfactants will be used to maintain performance. AOS and SAS I consider only as specialty chemicals and, therefore, foresee no appreciable effect that these products would have upon future LAS usage. The alcohol sulfate-ether sulfate mixture (LMES) should also grow because of hardness resistance and, therefore, I see the workhorses remaining the workhorses of the detergent industry.