The Selection of Surfactants for Specific Household Applications

MICHAEL F. COX and TED P. MATSON, Surfactant Applications, Chemicals Technical Service Division, Conoco Inc., Ponca City, OK 74601

ABSTRACT

The various criteria involved in choosing a surfactant for laundry products, light-duty liquids, shampoos and liquid soap products are discussed. These include cleaning performance, foam characteristics, formulatability, tolerance to water hardness, processability, and cost. The effect of surfactant composition on performance is also discussed.

Only major surfactants commonly used in the United States are included in this discussion. Due to lack of sufficient biodegradability, hard alkylate (alkyl benzene sulfonate) and alkylphenol ethoxylates are omitted. The major surfactant types included are linear alkylate sulfonates (LAS), alcohol nonionics (NI), alcohol ether sulfates (ES), alcohol sulfates (AS), and alpha olefin sulfonates (AOS). The 1981 consumption of these surfactants in the United States is shown in Table I.

The various criteria used in selecting a surfactant for an application are important. Since differing circumstances often dictate the relative importance of specific criteria, it is impossible to state which surfactant is best for each application. Therefore, before attempting the selection process, the relative importance of one's criteria must be clearly established.

LAUNDRY POWDERS

The most common laundry powder formulations use LAS, NI, or an LAS/AS/ES mixed-active surfactant system (1). Before discussing the selection of surfactants for laundry powders, the relationship between performance and composition for each surfactant type must be reviewed.

The molecular weight, or carbon chain length, of LAS is important in determining its detergency performance, as illustrated in Figure 1 for phosphate-built LAS homolog formulations. As shown, the detergency rating (measure of the detergency on cotton and permapress cloth) improves as LAS molecular weight is increased. This is true under low (50 ppm) and high (300 ppm) water hardness conditions as long as the formulations are properly built. When poorer builders are used, or in underbuilt formulations where nonsequestered hardness can deterimentally affect performance, the relationship between molecular weight and detergency can vary. In general, the higher molecular weight LAS materials (346 [C_{12}] to 362 [C_{13}]) are the most commonly used in laundry powders. Seldom will the lower molecular weight material (C_{11}) show superior detergency performance.

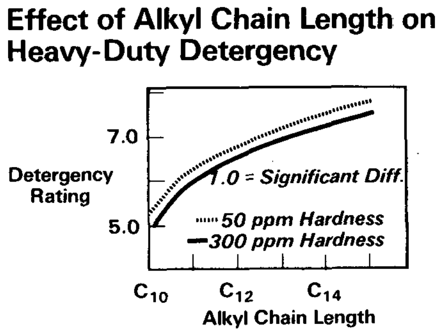

FIG. 1. The effect of alkylate chain length on detergency performance for LAS homologs (0.20% concentration, 50 and 300 ppm hardness, sebum soil).

In choosing a nonionic for a laundry product, one should consider the effect of both alcohol molecular weight and percentage of ethylene oxide. Figure 2 shows the detergency performance of alcohol nonionic as a function of varying alcohol molecular weight and percentage of ethylene oxide. The optimum lies between a C_{12} and C_{16} alcohol with 55-65% ethylene oxide. Different hardness or temperature conditions will make some marginal differences in the choice of the optimum performer.

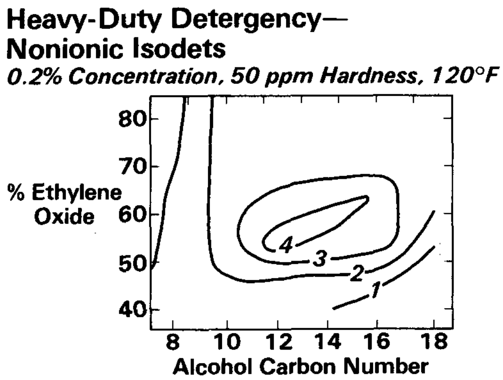

FIG. 2. Detergency optimization curves for alcohol nonionics as a function of alcohol molecular weight and percentage of ethylene oxide (10% NI, 30% STPP formulations; 0.2% concentration, 50 ppm hardness, sebum soil). (Larger isodet value = better detergency performance.)

Alcohol sulfates are known to be excellent detergents, but are sensitive to water hardness and show lower solubility (and performance) at cooler temperatures (2). Since detergent product trends have been toward lower washing temperatures and lower phosphate concentrations, the use of alcohol sulfates has declined. Alcohol ether sulfates also

TABLE I

Approximate 1981 US Consumption of Major Surfactants

Surfactant	US Consumption (million pounds)
Linear alkylate sulfonates (LAS)	750
Alcohol ether sulfates (ES)	290
Alcohol nonionics (NI)	280
Alcohol sulfates (AS)	240
Alpha olefin sulfonates (AOS)	25

Presented at the Feb. 24, 1982 meeting of the Southwest Section of the AOCS at Buena Park, California.

show good detergency performance, but due to their relatively high cost, they are not often used as primary detergent surfactants. However, blends of AS/ES in conjunction with LAS are used to provide a high-quality laundry product.

The detergency performances of alcohol sulfates and ether sulfates also depend upon their compositions. Figure 3 shows the effect of water hardness and temperature on the detergency performance for various molecular weight AS homologs. The optimum carbon chain length depends on the conditions, as shown, but is generally considered to be in the C_{14}-C_{16} range. The optimum ether sulfate composition is shown in Figure 4 to be a C_{14}-C_{16} alcohol with 25-45% ethylene oxide.

One important criterion which must be considered in choosing a surfactant system is processing. The available methods of producing the product, e.g., spray drying, agglomeration, or dry neutralization, may affect one's choice of surfactant. For example, although LAS, NI, and a mixed-active system can all be made by the spray-drying process, LAS is the usual choice based on processability and cost. A nonionic product can also be made by agglomeration onto or into inorganic materials, or (at lower active levels) by

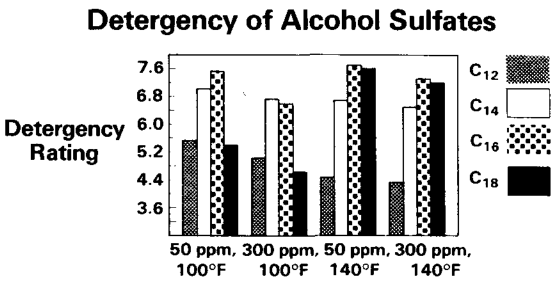

FIG. 3. Effect of water hardness and temperature on detergency of alcohol sulfate homologs (0.25% concentration, sebum soil).

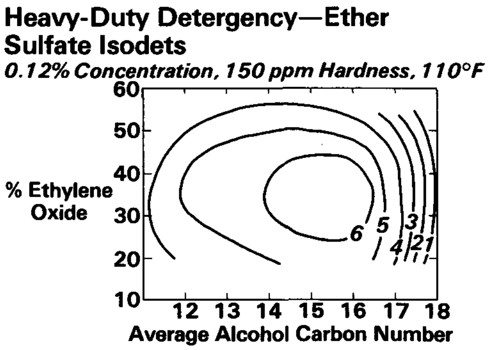

FIG. 4. Detergency optimization curves for ether sulfate homologs as a function of carbon chain length and percentage of ethylene oxide (0.12% concentration, 150 ppm water hardness, sebum soil).

overspraying a previously mixed remainder of the formulation. In addition to spray drying, an LAS product can be made from a sulfonic acid by simple dry-neutralization techniques. Therefore, the processing equipment, energy, and expertise available can limit the choices of surfactant systems.

Cost is another important criterion for surfactant selection. In general, the surfactants discussed are ranked in increasing cost: LAS, nonionic, ether sulfate, and alcohol sulfate. Keep in mind that cost considerations must include the expense of processing and handling the surfactant materials. Logically, a mixed-active system is more expensive to produce. Manufacturers can lower finished surfactant costs by performing a portion of the surfactant processing themselves. For example, LAS is available as the sulfonic acid, which is less expensive than the sulfonate, primarily since the material is nearly 100% active, whereas LAS is ca. 50% active, meaning one pays for shipping a 50% water product. Sulfonic acid is fairly simple to neutralize and does not require sophisticated handling and mixing equipment.

Keeping in mind the effects of chemical compositions upon performance and the processing methods available, one can begin to compare the relative performance of each of the major surfactants under consideration. All surfactant types show good detergency characteristics overall, but depending on the specific objectives of the product, differences are evident. LAS, for example, shows the optimum performance on particulate soil and sebum soil (typical body soil), while nonionics perform better on oily soils. LAS also gives better performance on certain synthetic fibers, such as Dacron, while nonionics perform well on Nylon.

Specific performance parameters can depend on where the product is aimed in the marketplace. For example, if high-foaming characteristics are desired, LAS or an LAS/AS/ES mixture would be used. If low foaming is required, a NI system would be chosen.

The effect of builder is also important. Since alcohol sulfates and LAS are more sensitive to water hardness, if a poor builder system were chosen, one might see advantages for an active system containing an ether sulfate or nonionic. However, it is usually less expensive to formulate with sufficient builder than to employ an alternative surfactant. Consequently, LAS and LAS/AS/ES active systems are the most popular.

The selection can be difficult, depending on the criteria and the magnitude of each selection guide established. The processing methods available, the builder type and level to be employed, and the performance and foaming characteristics of the product desired would logically make the selection of surfactant systems less complicated. Some examples of the variety of heavy-duty laundry powder formulation are given below in Table II.

LAUNDRY LIQUIDS

Selection of a surfactant is less difficult for heavy-duty liquids, primarily because the choice is limited by solubility and formulatability considerations. Three active types are commonly used in laundry liquids: LAS, LAS/NI, and ES/NI mixtures. The specific choice of surfactant is primarily dependent upon whether a built or nonbuilt formulation is desired. A built formulation can employ LAS or LAS/NI as the active material, and would contain tetrapotassium pyrophosphate (TKPP) or sodium citrate as the builder. In nonbuilt formulations, an LAS/NI mixture is the most common active used, although a major product currently contains a relatively expensive ES/NI active system. In addition, nonionic alone is sometimes used in formulations where anionic surfactants cannot be used, such as products containing quaternary salts as fabric softening agents. Since nonbuilt formulations do not contain builders, the concentration of the active is normally increased in order to maintain performance (3-5).

The optimum LAS for use in laundry liquids is the $C_{11/12}$ ($\sim$ 340) molecular weight material; primarily due

TABLE II

Typical Laundry Powder Formulations

	High foam			Low foam	
	I	II	III	IV	V
Percent LAS	15-20	20-25	7	–	–
Percent NI				8-14	8-14
Percent AS			7		
Percent ES			7		
Percent sodium tripolyphosphate (STPP)	25-35		25-35	25-35	
Percent sodium carbonate		30-50			40-50
Percent sodium silicate (rust inhibitor)	5-10	5-10	5-10	5-10	5-10
Percent antiredeposition agent	0-2	0-2	0-2	0-2	0-2
Percent sodium sulfate, whitening agent, color, perfume, etc.	qs	qs	qs	qs	qs

to solubility. However, the optimum nonionic depends on whether the product is nonbuilt or built, and upon the type of soil used in evaluating its detergency. The optimum nonionic in a built heavy-duty liquid is usually based on a C_{12}-C_{14} alcohol containing ca. 55-65% ethylene oxide. The optimum nonionic in a nonbuilt formulation is shown in Figure 5 to be made from a C_{12}-C_{16} alcohol with a 60-80% ethylene oxide adduct when tested on sebum-soiled cloth. However, when tested on motor oil-soiled cloth, as shown in Figure 6, the optimum is shifted to a more narrow band centered around a C_{13} alcohol with 60% ethylene oxide.

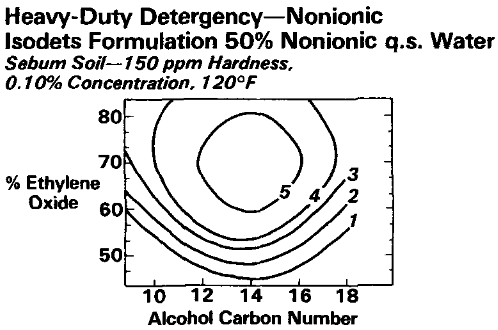

FIG. 5. Detergency optimization curves on sebum-soiled cloth for nonionic as a function of alcohol carbon chain length and percentage of ethylene oxide (50% NI in H_2O, 150 ppm water hardness).

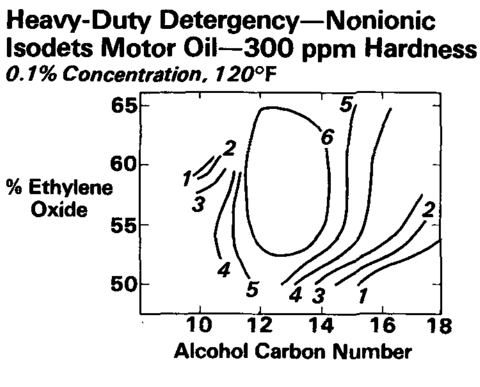

FIG. 6. Detergency optimization curves on motor oil-soiled cloth for nonionic as a function of alcohol carbon chain length and percentage of ethylene oxide (50% NI in H_2O, 300 ppm water hardness).

For nonbuilt products, the optimum performing ratio of LAS to NI in LAS/NI mixtures again depends on the parameters used to evaluate the products performance, especially the soil type. For example, if the optimum detergency on sebum and particulate soil is desired, then a high LAS to NI ratio would be used, while a low ratio would be employed for optimizing the detergency on oily soils. Examples of built and nonbuilt heavy-duty liquid formulations are given in Table III.

TABLE III

Typical Built and Nonbuilt Laundry Liquid Formulations

Built	Nonbuilt	
I	II	III
LAS/NI	LAS/NI	NI/LAS
10% alkylbenzene sulfonate	25-35% LAS	10% LAS
0-15% nonionic	10-15% nonionic	30-35% nonionic
10-20% TKPP or citrate	5-10% solubilizer	5-15% solubilizer
5-10% hydrotrope	40-60% H_2O	45-55% H_2O
qs H_2O		

The formulatability (ease of reaching viscosity and stability requirements) also depends on the composition of the active chosen. For example, the addition of LAS to a nonionic solution typically increases the stability of the formulation. Another example is the solubility (cloud/clear point) advantages of a 70% ethylene oxide nonionic vs a 60% EO adduct (4-7).

As indicated in the previous discussion, before selecting a surfactant for a laundry liquid product, one must decide on whether the product will be built or nonbuilt. Built formulations usually outperform comparable nonbuilt formulations but are more difficult to formulate, mainly due to the influence of the builder upon the solubility and stability of the other components. On the other hand, nonbuilt products are easier to formulate and give relatively few problems with respect to stability as long as they are properly made (6-9).

The relative costs of nonbuilt and built formulations depend only partially upon the cost of the active(s) and builder. Other cost considerations must include the intended use level of the product, the concentration of the active, and the cost of the other ingredients such as hydrotropes, viscosity builders, etc. However, an active consisting of a high LAS/NI ratio is the preferred choice in terms of both cost and performance.

LIGHT-DUTY LIQUIDS

Two major active systems are commonly used in dishwashing liquids; LAS/ES and AS/ES mixtures. Nonionics are not typically used in light-duty liquids because they are lower foamers and are believed to degrease the skin, causing "dishpan hands." Alpha olefin sulfonates (AOS) were at one time used in a major light-duty liquid, but are no longer found in any major product.

The mixed-active systems, LAS/ES and AS/ES are by far the most common actives used in LDL because of their superior performance. LAS can be used alone in LDL formulations, but because there exists an LAS/ES synergism, it is usually used in conjunction with ether sulfate. Figure 7 illustrates the LAS/ES synergism, where the performance of the LAS plus ES mixture is superior to that of the sum of the individual performances of LAS and ES. The performance was determined by standard dishwashing tests and is described by the number of plates which can be washed before the foam is exhausted. As shown, the optimum LAS/ES ratio is ca. 5/1. Consequently, LAS/ES is popular since the synergism increases the cost/performance efficiency of the mixture. The optimum LAS molecular weight, as shown in Figure 8, has about a C_{11}-C_{12} average carbon chain length (10). The best ether sulfate is considered to be made from a C_{12}-C_{14} alcohol ethoxylate with ca. 40% ethylene oxide.

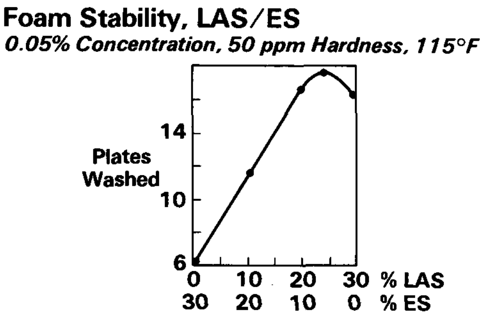

FIG. 7. Effect of LAS/ES ratio on foam stability (0.05% concentration, 50 ppm hardness).

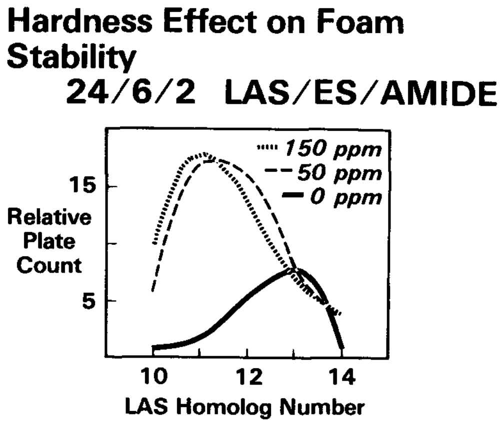

FIG. 8. Effect of LAS molecular weight on foam stability (24% LAS/6% ES/2% amide formulation; 0.05% concentration).

The optimum ratio of AS/ES, based on cost/performance, is usually determined by the relatively high expense of the surfactants. Normally, the ratio of alcohol sulfate to ether sulfate is very low.

In choosing surfactants for dishwashing liquids, one is primarily interested in the foam stability (performance), formulatability, and cost of the formulation. All formulations generally show lower foam stability in exceptionally soft water. Consequently, some manufacturers add inorganic magnesium salt to the formulation. At high hardness, LAS formulations excel in foam stability performance. In addition to the surfactants, a foam stabilizer is added to the formulation, such as an alkanolamide (in LAS/ES formulations), or an amine oxide (in AS/ES formulations).

With respect to cost, the alcohol sulfate/ether sulfate formulation is obviously more expensive to produce, because of both the cost of the surfactants and the expense of the amine oxide foam stabilizer, which is superior in AS/ES formulations. In LAS/ES formulations, less expensive foam stabilizers, alkanolamides, are found to be the optimum choice. Consequently, LAS/ES formulations are the more popular choice to produce.

Another criterion for surfactant selection is the formulatability. Restrictions on viscosity and cloud/clear point (stability requirements) determine the amount of hydrotrope or thickener which must be added to the formulation. The viscosity and solubility requirements are affected by both the surfactant type and the formulation.

Dishwashing liquids are rather easy to process, requiring simple mixing equipment. One should choose the surfactant system based on surfactant availability and performance specifications, and then optimize the formulation with respect to cost. Several typical light-duty liquid formulations are shown in Table IV.

TABLE IV

Typical Light-Duty Liquid Formulations

Type I	Type II	Type III
15-25% LAS	16-28% LAS	20-30% AS/ES
0-5% fatty amide	2-12% ES	3-5% amine oxide
0-10% urea (viscosity builder)	2-5% fatty amide	6-10% EtOH
SXS as needed	3-7% SXS	qs H_2O
qs H_2O	qs H_2O	

SHAMPOOS AND LIQUID SOAPS

Since the ultimate objective of formulating both shampoos and liquid "soaps" is to produce a mild product which makes thick, copious foam, especially in the presence of sebum soil, the methodology involved in selecting surfactants for them will be discussed together. The primary types of actives generally used are alcohol sulfates and ether sulfates. Alpha olefin sulfonates are also used in liquid hand soaps and in shampoos. LAS has also been formulated into inexpensive liquid hand soaps.

Alcohol sulfates are most often used in these products because they provide exceptionally thick foam that is stable over a wide range of soil concentrations. The optimum alcohol sulfate carbon chain length is considered to be in the C_{12}-C_{14} (lauryl) range. Low-mole ether sulfates, which are alcohols which have been ethoxylated to a 1-3 mole average prior to sulfation, also provide good foam characteristics. The optimum percentage of ethylene oxide is difficult to determine, primarily because the lower the percentage, the better the foam characteristics, while higher percentages of EO yield more soluble and milder surfactants.

Alpha olefin sulfonates can also be found in some liquid soaps and shampoos. AOS provides good foam, but the quantity and stability of the foam is substantially less when compared to alcohol sulfate, especially at higher use level concentrations and when soil is present during testing (11,12). Figures 9 and 10 illustrate the relative quantities and stabilities of foam generated artificially for a lauryl-range alcohol sulfate and AOS. The more desirable foam qualities for these products are the production of large amounts of thick, copious foam which is stable (high-drainage time).

The actual cleaning performances of the various surfactants discussed above are difficult to measure, but are considered relatively equal. Of seemingly more importance is the quantity, quality, and stability of the foam produced. Consequently, foam stabilizers, such as amides or amine oxide are often added to the formulation.

Other criteria needed to select a surfactant for these types of products should also include solubility, overall formulatability, and cost. Normally, the market requirements for the product, such as mildness, concentration, odor, etc., often complicate the decision. Also, the formulatability of a particular surfactant depends on the "formula." With respect to cost, alpha olefin sulfonates are less expensive than alcohol sulfates and ether sulfates. However, when cost/performance is considered, alcohol sulfates are least expensive, followed by ether sulfates and AOS.

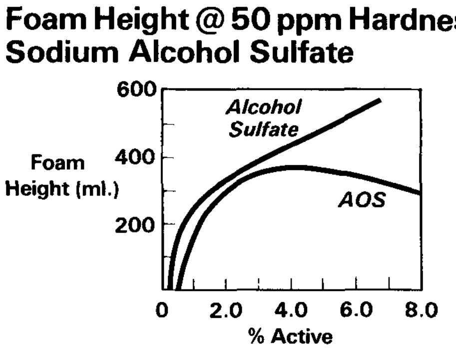

FIG. 9. Foam height as a function of surfactant concentration for alcohol sulfate and AOS (50 ppm hardness).

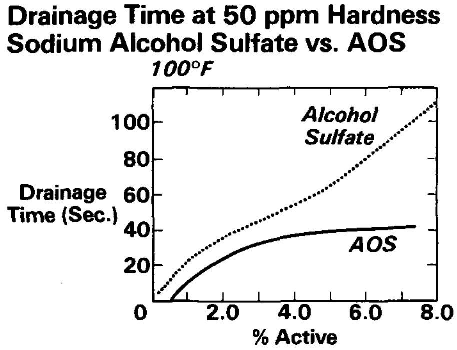

FIG. 10. Foam drainage time as a function of surfactant concentration for alcohol sulfate and AOS (50 ppm hardness).

REFERENCES

1. Matson, T.P., in Monohydric Alcohols, edited by E.J. Wickson, American Chemical Society, Symposium Series 159, 1981.
2. Matson, T.P., JAOCS 40: 640 (1963).
3. McGuire, S.E., and T.P. Matson, JAOCS 52: 11 (1975).
4. McKenzie, D.A., JAOCS 55: 93 (1978).
5. Dillan, K.W., E.D. Goodard, and D.A. McKenzie, JAOCS 56: 59 (1979).
6. Matson, T.P., and M. Berretz, Soap Cosmet. Chem. Spec. 55: 33 (1979).
7. Matson, T.P., and M. Berretz, Ibid. 55: 41 (1979).
8. Matson, T.P., and M. Berretz, Ibid. 56: 36 (1980).
9. Matson, T.P., and M. Berretz, Ibid. 56: 41 (1980).
10. Stanberry, C.J., T.P. Matson and J.J. Langford, Ibid. 40: 43 (1964).
11. Borys, N.F., and T.P. Matson, Paper presented at 72nd Annual AOCS Meeting, New Orleans, May 1981.
12. Matson, T.P., JAOCS 55: 66 (1978).