Review of Alkylaryl Sulfonates[1]

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THE SYNTHETIC DETERGENT industry has in the last 20 years enjoyed a phenomenally rapid growth. This growth has been from a negligible .07% of the surfactant market in 1935 to a very substantial 63.2% of the market in 1955, as recently reported by the Association of American Soap and Glycerine Producers. Even as recently as 1947 the synthetics represented only 10% of the total surfactant market.

Paralleling this rapid growth has been the growth of the alkylaryl sulfonates, often called the "workhorse" of the synthetic detergents, which are the subject of this paper.

Alkylaryl sulfonates are classified as anionic compounds like soap, as distinguished from cationic and nonionic. The alkylaryl sulfonates are products derived from the sulfonation of alkylaryl hydrocarbons, commonly called detergent alkylates, and were first developed in Germany in the early 1930's. These early alkylates were produced by the alkylation or aromatics, such as naphthalene and benzene, with chlorinated paraffins. These paraffins were obtained by distillation of petroleum stocks from eastern Europe. This type alkylate is known as keryl benzene. Sulfonation of the alkylate yields sulfonates possessing good detergency and wetting properties and, as such, have found good acceptance as an industrial detergent. The main industrial usage was and still is in the textile industry, where they are used in wool scouring and wetting. These sulfonates are sold normally as drum-dried products of approximately 40% active sulfonate and 60% sodium sulfate. Other forms include pastes, gels, and liquids.

About 1932 interest was being shown in the United States in this type of synthetic surfactant. One or more companies through their own research efforts and licensing agreements with I. G. Farben began to manufacture and market some keryl-benzene sulfonates for industrial usage. These products found good acceptance in the textile industry as well as a number of other industries and the production of the sulfonates grew from 3.5 million pounds of 100% active in 1939 to 46 million pounds in 1946. Since the alkyl sulfonates have also found wide acceptance in the household field, this production has grown from 46 million pounds in 1946 to 389 million pounds in 1954 and 449 million pounds in 1955 as reported by the U. S. Tariff Commission.

While the keryl-benzene sulfonates were being used widely in industrial applications, they were not used to any degree in the household detergent field until after World War II. Reasons for this were poor odor and color unless extensively purified and lack of suitable formulations to satisfy the soap industries' requirements for quality.

SINCE WORLD WAR II the alkylaryl sulfonate type surfactant has enjoyed its most rapid growth as the result of its being incorporated into products for the household surfactant field. Two important reasons for the alkylaryl sulfonates' invasion of the household field were: a) the development of tetrapropylene (also called dodecene) as a replacement for kerosene and the resultant production of dodecylbenzene, which provided the manufacturer with a low-cost, high-quality, raw material having unlimited availability and good price stability; the utilization of dodecene in the production of the alkylate makes it possible more closely to control the uniformity of the alkylate as well as yield a product that is quite resistant to degradation upon sulfonation; and b) the development of formulations, using phosphates and other builders, to give products having excellent detergency and foam in both soft and hard water.

In a paper discussing the development of alkylaryl sulfonates it seems fitting that a brief discussion of their manufacture from beginning to end should be included. Since the dodecylbenzene type alkylaryl now comprises probably 90% or more of the total production of the alkylaryl sulfonates, its process of manufacture will be discussed.

Before discussing the manufacture of alkylaryl sulfonates, it is well to examine the standards of quality for the finished sulfonated product. Recent improvements in the quality of detergent alkylates and sulfonation techniques have resulted in an exacting quality standard for household and industrial products alike. Although the requirements of each type of product vary and each application presents special problems, it is possible to generalize to some extent. Some of the more important properties relating to the quality of detergent alkylate sulfonates are given in Table I for the purpose of illustration.

TABLE I

Example of Quality Requirements for Detergent Alkylate Sulfonates

Property	Standard
Color	Paper white without bleaching
Odor	Minimum: must not develop with age
Unsulfonated hydrocarbon	Must not exceed 2% and may be as low as 1%, based on active agent. For extracted products this may be reduced to 0.5%, based on active agent
Performance	Must equal standards for foam, wetting, detergency, solubility, and compatibility with builders
Drying	Formulated slurries of high solids content must be fluid and pumpable and should spray and drum-dry to free-flowing solids
Packaging	Free-flowing, non-tacky, minimum dusting in packaging operation and non-caking in the package under humid conditions

The basic reactions of the manufacturing process are, briefly, the polymerization of propylene to "dodecene," sulfonation of the alkylate with sulfuric acid, and neutralization of the sulfonic acid with the desired base.

Roughly a 50-50 propane-propylene stream from a catalytic cracking unit, from which the butylenes have been removed, is fed to a catalytic polymerization unit. It is extremely important that the feed stream be free of butylenes (less than 0.5%) because their presence will give a polymer that is unstable to both alkylation and sulfonation. The desired "dodecene" cut is obtained by distillation, and the lower boiling hydrocarbons are recycled to the unit along with a fresh propane-propylene feed. Quality control of the "dodecene" is based on such physical tests as bromine number, A.S.T.M. distillation range, and infrared analysis.

Benzene is available from both the petroleum industry and the coal tar industry. Petroleum benzene is made by a reforming operation such as hydroforming or platforming of light naphthas.

The alkylation step involves the reaction of an aromatic hydrocarbon with an olefin by the Friedel-Crafts reaction. Friedel-Crafts catalysts most commonly used in this alkylation are either aluminum chloride, hydrogen fluoride, or sulfuric acid. The three principal variables of this alkylation reaction are molar ratio of aromatic to olefin, reaction temperature, and catalyst concentration. Since an excess of aromatic hydrocarbon (benzene) is used and the reaction product consists of a mixture of alkylaryl hydrocarbons of varying molecular weights, an extensive distillation step is required to obtain the desired alkylaryl hydrocarbon.

Table II lists the typical physical properties of a present-day dodecylbenzene alkylate. This alkylate contains more than 99% alkylbenzenes, which are predominately monosubstituted, although traces of disubstitution are indicated by infrared. It is interesting to note that continued efforts to improve the quality of dodecylbenzene over the past six years has resulted in today's product having a considerably narrower boiling range.

TABLE II

Typical Physical Properties of Dodecylbenzene

A.S.T.M., D-158 Engler distillation range °F.	
I.B.P.	535
5%	545
50%	560
97%	593
F.B.P.	603
Specific gravity @ 60°F.	0.8742
Apparent M. W.	237–240
Aniline pt.	48.5
Bromine No.	0.16
Saybolt color	29
Centipoise V.S. @ 68°F.	14
Refractive index @ 68°F.	1.4885
Appearance	Clear and water-white
Flash COC	260°F.

THE PURPOSE of sulfonation is to achieve a product with the proper balance of water solubility for the desired surface-activity in water systems. This is accomplished by combining the water-soluble (hydrophilic) sulfonic acid group with the water-insoluble (hydrophobic) detergent alkylate. In the simplest terms this is done either continuously or batch-wise by vigorously agitating a two-phase mixture of detergent alkylate and a molar excess of strong sulfuric acid. The excess sulfuric acid is necessary to gain essentially 100% sulfonation of the hydrocarbon. The three principal strengths of sulfuric acid used are 98%, 100.5%, and 104.5%. During the past few years considerable interest has been shown for use of sulfur trioxide gas diluted with dry air. The temperature of the exothermic reaction is carefully controlled to prevent discoloration and formation of odor-producing bodies that result from scorching and other side-reactions. The most important variables of sulfonation are: strength of sulfonating agent, ratio of sulfonating agent to detergent alkylate, sulfonation temperature, technique and time of addition of sulfonating agent, degree of agitation, temperature and time of aging the sulfonation reaction mass, and the technique of neutralization of the sulfonic acid. Though not commonly considered a variable, the purity of the sulfonating agent and the base used in the neutralization is of critical importance. In particular, iron contamination affects the color of the sulfonate. Sulfonations are generally carried out in nickel-chromium alloy steels or glass-lined equipment.

In neutralizing the sulfonic acid several routes may be followed, depending on the desired final product. Basically there are two types of products produced, commonly called low-active sulfonate and high-active sulfonate. The low-active sulfonate, 40% to 50% active, is produced by neutralizing the sulfonation mass, including the excess sulfuric acid, with the desired basic aqueous solution. The most common base used is caustic (sodium hydroxide). In this operation the sulfonation mass is added to the agitated, aqueous alkali and the rate of addition controlled so as to maintain the desired temperature of the mixture. The resultant neutralized product is commonly called "slurry." The neutralization is normally carried out in stainless steel equipment.

To produce the high-active sulfonate, 85% to 90% active, it is first necessary to dilute the excess sulfuric acid in the sulfonate mass to approximately 78% strength by the addition of the proper amount of water. The mixture is then allowed to separate, and the heavier spent acid layer (sulfuric acid) is removed from the sulfonic acid layer. This sulfonic acid layer normally contains about 10% of a 78% strength sulfuric acid and is then neutralized with the desired aqueous alkali solution in the same manner as the low-active sulfonate. The most commonly used base to produce high-active sulfonates is caustic, but ammonia and alkanolamines are also used when liquid products are desired.

The neutralized, low-active sulfonate slurry is most commonly adjusted to a 40% activity by the addition of sodium sulfate, and the slurry is drum-dried or spray-dried to either a flake or bead form.

The neutralized, high-active sodium sulfonate slurry is most commonly built with such builders as phosphates, silicates, amides, and carboxyl methyl cellulose; and the resultant slurry is spray-dried to yield a heavy-duty household detergent.

Another important use of the high-active sulfonate slurry is for use in household light-duty liquid formulations. For this use it is generally desirable to have less than 2% inorganic salts, based on the sulfonate present in the final product, which means that it is necessary to desalt the high-active sulfonate slurry. This is normally accomplished by employing an alcohol-extraction process. This alcohol-extraction process can be eliminated when sulfur trioxide gas is used as the sulfonating agent since the sulfonate from this process can be produced so as to have 2% or less inorganic salts in the neutralized product.

HAVING DISCUSSED the manufacture of alkylaryl sulfonates, it seems fitting to discuss briefly their present-day applications. Basically their applications are divided into two classifications for convenience: a) industrial detergents and wetting agents, and b) household detergents.

As previously mentioned, the alkylaryl sulfonates were originally developed for industrial use mainly in the textile industry. Today they are used in many industrial cleaning applications in a large number of industries. The two main forms in which they are sold as industrial cleaners today are a) 40% active drum-dried flake and b) 50% active triethanolamine neutralized liquid product.

The use of alkylaryl sulfonates in the household detergents began shortly after World War II and was the start of what has proven to be by far their largest use. The three main types of household detergents utilizing these sulfonates are a) spray-dried, heavy-duty detergents for general household laundry, b) spray-dried, light-duty detergents for washing of fine fabrics and dishes, and c) light-duty, liquid detergents for washing of fine fabrics and dishes. Thus, because of their low cost and excellent use properties, they have become the "work-horse" of the synthetic detergent industry.

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Fatty Alcohol Sulfates

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THE FATTY ALCOHOL SULFATES represent an important item of commerce and also are among the earliest detergents to be discovered and introduced. The first alcohol sulfate was prepared by Dumas in 1836. Almost 100 years later, in 1932, the alcohol sulfates were incorporated in the first successful retail detergent in the United States. Now, a quarter century later, they remain of very significant commercial importance.

Since long chain alcohols with carbon chain lengths varying from C_6 to C_{22} can be derived from various fats and oils, it is necessary to limit the discussion to a few materials which are readily available and of substantial commercial importance. This essentially limits the discussion to the alcohols from four sources, insofar as detergents are concerned, namely: coconut oil, palm kernel oil, tallow, and sperm oil.

For uses other than surface-active agents, castor oil and perhaps other fat-derived alcohols are of some importance, but these by common usage are normally excluded from the category of "fatty alcohol sulfates." The synthetic alcohols, which are beginning to find favor for some use as their ethoxylated derivatives, will not be included in the discussion since they are not fat-derived.

The approximate composition of three of the four fats mentioned above are shown in Table I.

TABLE I

Fatty Acid Content of Common Fats Used in Fatty Alcohol Production

Usual percentage of fatty acid	Coconut oil	Palm kernel oil	Tallow [a]
Caproic (C_6)	0–0.8	Trace	—
Caprylic (C_8)	5.5–9.5	3–4	—
Capric (C_{10})	4.5–9.5	3–4	—
Lauric (C_{12})	44–52	46–52	—
Myristic (C_{14})	13–19	14–17	6.3
Palmitic (C_{16})	7.5–10.5	6.5–9	27.4
Stearic (C_{18})	1–3	1–2.5	14.1
Oleic (C_{18})	5–8	13–19	49.6
Linoleic (C_{18})	1.5–2.5	0.5–2	2.5

[a] Bailey—North American Beef Tallow.

The typical lauryl alcohol of commerce as used in the production of lauryl sulfates is the hydrogenated coconut oil type with a portion of the lower boiling and of the higher boiling components removed.

Sperm oil represents a different situation from that of the previous three materials in that the alcohols themselves are derived from sperm oil since they are present in the oil as their esters. A typical saponified sperm oil will yield alcohols (Table II).

TABLE II

Fatty Alcohol Identity in Sperm Whale Head Oil

	Percentage [a]
Cetyl alcohol	50
Palmitoleyl alcohol	10–12
Stearyl alcohol	10–12
Oleyl alcohol	25
C_{20} alcohols	Remainder

[a] Of alcohol present.

Manufacture of Fatty Alcohols

There are moderate quantities of sperm oil alcohols used in this country. Some of these are manufactured domestically, but the large proportion are imported from Europe, where they are obtained by the saponification of sperm oil or spermaceti. In addition to this production by saponification, there are two generally used methods for producing higher fatty alcohols commercially: high-pressure hydrogenation and reduction with metallic sodium.

The choice of methods for producing higher fatty alcohols depends upon many factors which we do not have sufficient space to discuss fully. Briefly the hydrogenation process involves a large capital investment and is limited to producing saturated fatty alcohols since under most conditions of hydrogenation the double bonds are saturated. For some applications unsaturated alcohols, such as oleyl alcohol, are more desirable than the saturated alcohols, and sodium reduction must be used. Hydrogenation is also versatile however in that fatty acids, in addition to the various fatty acid esters, can be used as starting materials. The glyceryl esters are not normally used in this operation since the glycerine is further hydrogenated to propylene glycol and in some cases to isopropyl alcohol. It is more common practice to recover the glycerine from the glyceride first by means of fat splitting or ester interchange. The hydrogenation operation is then carried out, using the fatty acids or the methyl esters. Because of the drastic conditions employed (3,000 to 5,000 psi and 200° to 400°C.) in hydrogenation, there can also be formed an appreciable amount of hydrocarbon, which represents a loss of product yield and can alter the properties of the fatty alcohol derivatives.

The sodium reduction process does not normally represent as large an investment as the hydrogenation method. It is more flexible in that both saturated and unsaturated alcohols can be produced. However, in producing saturated tallow alcohols, for example, the tallow must first be hydrogenated before being