SULFONATION AND SULFATION

1. Introduction

Sulfonation and sulfation, chemical methods for introducing the SO_3 group into organic molecules, are related and usually treated jointly. These methods are utilized widely throughout the world and are important chemical processes for manufacture of a number of product classes, including surfactants, polymers, dyes, concrete additives, pesticides, and medicinals. In the anionic surfactant industry alone, it is estimated that ~139 plants across the globe had an sulfonation capacity (in terms of linear alkylbenzene sulfonates) of 4.9 million metric tons as of 2003 (1). Of this capacity, 1.5 million metric tons resided in North America (United States, Canada, Mexico).

In sulfonation, an SO_3 group is introduced into an organic molecule to give a product having a sulfonate, CSO_3, moiety. This product may be a sulfonic acid, a salt, or a sulfonyl halide requiring subsequent alkaline hydrolysis. Aromatic hydrocarbons are generally directly sulfonated using sulfur trioxide, oleum, or sulfuric acid. Sulfonation of unsaturated hydrocarbons may utilize sulfur trioxide, metal sulfites, or bisulfites. The latter two reagents produce the corresponding hydrocarbon metal sulfonate salts in processes referred to as sulfitation and bisulfitation, respectively. Organic halides react with aqueous sodium sulfite to produce the corresponding organic sodium sulfonate. This is the Strecker reaction, also referred to as sulfonato-de-halogenation. In instances where the sulfur atom at a lower valance is attached to a carbon atom, the sulfonation process entails oxidation. Thus the reaction of a paraffin hydrocarbon with sulfur dioxide and oxygen is referred to as sulfoxidation; the reaction of sulfur dioxide and chlorine is called chlorosulfonation. The sulfonate group may also be introduced into an organic molecule by indirect methods through a primary reaction, eg, esterification, with another organic molecule already having an attached sulfonate group.

Sulfation is defined as any process of introducing an SO_3 group into an organic compound to produce the characteristic $C{-}OSO_3$ configuration. Typically, sulfation of alcohols utilizes chlorosulfonic acid or sulfur trioxide reagents. Unlike the sulfonates, which show remarkable stability even after prolonged heat, sulfated products are unstable toward acid hydrolysis. Hence, alcohol sulfuric esters are immediately neutralized after sulfation in order to preserve a high sulfation yield. In addition, sulfated products are prone to hydrolysis under strongly alkaline conditions, which can limit the utility of such products in favor of sulfonate alternatives.

In sulfamation, also termed *N*-sulfonation, compounds of the general structure R_2NSO_3H are formed as well as their corresponding salts, acid halides, and esters. The reagents are sulfamic acid (amido–sulfuric acid), SO_3–pyridine complex, SO_3–tertiary amine complexes, aliphatic amine–SO_3 adducts, and chlorine isocyanate–SO_3 complexes (2).

2. Uses for Derived Products and Sulfonation Technology

Sulfonation and sulfation processes are utilized in the production of water-soluble anionic surfactants, which are principal ingredients in formulated light-duty and heavy-duty detergents, liquid hand cleansers, combo bar soaps, general household and personal care products, and dental care products (see DENTIFRICES). Generally, household and personal care products must have light color, little unreacted material (free oil), low inorganic salt, and negligible odor. Bleach activators represent an additional commercial sulfonate technology. Sulfonated and sulfated products for industrial applications include emulsifiers for emulsion polymerizations, pesticide–herbicide emulsifiers, concrete additives, demulsifiers, textile wetting agents, dry-cleaning detergents, leather tanning agents, metal cleaners, corrosion inhibitors, and oil-production chemicals. Other commercially significant product sectors include lube additives, pesticide chemicals, medicinals, sweeteners, cyclic intermediates, dye and pigment products, and ion-exchange resins. This latter class of materials finds uses as strong acid catalysts and as ion-transport membranes in the exanding field of fuel cell technology.

Application chemists are most interested in physical and functional properties contributed by the sulfonate moiety, eg, solubility, emulsification, wetting, foaming, detersive properties, and chemical acidity. Products can be designed to meet various criteria including water solubility, water dispersibility, and oil solubility. The polar SO_3 moiety contributes detersive properties to lube oil sulfonates and dry-cleaning sulfonates.

2.1. Process Selection and Options.

Because of the diversity of feedstocks, no single process fits all needs. An acceptable sulfonation/sulfation process requires (*1*) the proper reagent for the chemistry involved and the ability to obtain high product yields; (*2*) consistency with environmental regulations such that minimal and disposable by-products are formed; (*3*) an adequate cooling system to control the reaction and to remove significant heat of reaction; (*4*) intimate mixing or agitation of often highly viscous reactants to provide adequate contact time; (*5*) products of satisfactory yields and marketable quality; and (*6*) acceptable economics. Sulfonation and sulfation processes have been recently reviewed (3).

Elevated viscosity can play a significant role in dictating agitation/mixing requirements and can also seriously affect heat-exchange efficiency. For example, in the case of SO_3 sulfonation of various surfactant feedstocks, viscosity generally undergoes a 15- to 350-fold increase on reaction, significantly reducing heat-transfer coefficients. Conventional continuous sulfonation equipment, eg, falling film reactors, are generally suitable for producing sulfonic acid products with viscosities up to ~ 1500 cps, whereas some industrially important products may have viscosities as high as 40,000 cps (4). In some instances, where the feedstock has a high melt point or where either the feedstock or its sulfonic acid exhibits high viscosity under nominal sulfonation reaction temperatures, the use of higher temperature cooling media, eg, hot water or steam cooling has been utilized (4). In addition, the application of a pressure drop to accellerate gaseous SO_3 across the length of a falling film tube reactor has been reported to be effective in overcoming viscosity limitations (4).

Sulfonation reactants and reaction products may be miscible or immiscible. For example, the reagents in sulfuric acid sulfonation of simple aromatic hydrocarbons, eg, xylenes, are immiscible and therefore mixing has important effects on reaction kinetics. In some instances, "inert" solvents may be required to overcome high viscosity, poor heat transfer, or reagent incompatability; examples of useful solvents include pentane, methylene chloride, and liquid sulfur dioxide.

2.2. Industrial Changes Affecting Sulfonation–Sulfation Operations. Ongoing changes dating to the 1980s that impact sulfonation–sulfation operations on a worldwide basis include maturation of the sulfonation industry and its technology, development of a highly competitive and reactive market environment, and environmental and safety regulations affecting the types of manufacturing operations, plant locations, by-product generation and disposal, plant emissions, and other discharge streams. Sulfur trioxide has become the dominant sulfonation reagent for anionic surfactant manufacture, largely though not completely supplanting oleum sulfonation processes. For example, a Huish SO_3-air sulfonation plant with 79,000 metric ton annual capacity came on stream in Texas in 2003, concurrent with a shut-down of the company's 8000 metric ton oleum sulfonation plant in Wyoming (1). The preference for SO_3-based sulfonation is particulary strong amongst merchant manufacturers of surfactants, where manufacturing flexibility is critical to plant rationalization and adaptable product mixes. Continuous falling film SO_3 sulfonation continues to be the method of choice for sulfonating liquid flowable feedstocks, and improvements in raw material quality (5) and reactor design have enabled further optimization of product quality (6).

Shifting consumer preference for liquid laundry detergents over powders in the United States, significant cost pressures on detegent manufacturers from discount retailers, and advances in detergent formulation technologies, eg, advanced enzymes and bleaching systems have all had a significant impact on the anionic surfactant industry. A dramatic shift away from linear alkylbenzene sulfonates (LAS) to alcohol ethoxylate sulfates (AES) in North American laundry detergents occurred during the 1990s and has held firm through the first half of the 2000s (7). Particularly in Europe, concerns over trace 1,4-dioxane content in AES continues to drive improvements in alcohol ethoxylate sulfation technology (3). As of 2005, volatility in the petroleum market has intensified interest in anionic surfactant technologies that utilize nonpetroleum based feedstocks, eg, methyl ester sulfonates (MES) derived from palm oils. Developments and potential future developments in anionic surfactant feedstocks has been reviewed (8).

Production of dyes and dye intermediates, including the sulfonation opperations associated with this production, has declined signficantly over the past decade in North America and Europe as production has largely been relocated to Asian countries, eg, China and India. Severe price pressures have resulted from oversupply of dyestuffs, and competition from small producers has forced large dyestuff manufactures to restructure (9). Sulfonated products for use in lubricants and metalworking likewise suffered from a decline in value in the early 2000s due in part to competition from producers in China and India (10).

3. Economic Aspects

It was estimated from U.S. International Trade Commision reports that in the United States during 1991, $\sim 1.92 \times 10^6$ metric tons of sulfonated, sulfated, and sulfamated products were manufactured. This represented a market value of $\sim$ $\$3.4 \times 10^9$ and constituted $\sim$4.5% of the annual value of all synthetic organic chemical production. Anionic surfactants comprised 79.2% of the total estimated volume of sulfonated products in the United States in 1991, representing 49.2% on a total products value basis.

In 1996, the U.S. government stopped collecting synthetic organic chemicals data, so comprehensive statistics are not readily available for more recent years. However, Table 1 provides product volume estimates and list pricing in the time period of 2001–2004 for several classes of sulfonated and sulfated products in the United States. Total North American consumption of sulfonate and sulfate anionic surfactants in 2003 (excluding lignosulfonates) was 1.18 million metric tons. The largest use category for anionic surfactants is in household detergents. While U.S. consumption of anionic surfactants for consumer luandry detergents increased considerably in the 1990s, driven largely by the higher surfactant levels in liquid products, a subsequent slight decline in consumption occurred in the early 2000s. Total North American consumption of anionic surfactants declined as well during this same period. As of 2005, the anionic surfactants market in Western Europe continues to suffer from sulfonation overcapacity. The U.S. consumption of lignosulfonates declined by 29% from 1994 to 2001, and most lignosulfonate components from sulfite pulp mills are burned for fuel value (11).

4. Reagents

Reagents for direct sulfonation and sulfation reactions are listed in Table 2, arranged according to perceived relative reactivity. The data includes 2005 U.S. costs, number of manufacturers, general usage, advantages, disadvantages, and applications. Since Fremy first batch-sulfonated olive oil with sulfuric acid in 1831 (15), sulfonation and sulfation reactions had mainly been conducted using sulfuric acid or oleum reagents. Each requires the use of several moles of reagent per mole of feedstock. However, chlorosulfonic acid and SO_3 react stoichiometrically, and have therefore gained preferred commercial acceptance.

By 1987, sulfur trioxide use in the United States exceeded that of oleum for sulfonation. It has been reported that as of 1999, U.S. detergent manufacturers that produce linear alkylbenzene sulfonates for captive use were operating only five oleum plants (1). Sulfur trioxide sources are divided between liquid SO_3 and *in situ* sulfur burning. The latter is integrated into sulfonation production facilities.

Liquid SO_3 is commercially available in both unstabilized and stabilized forms. Unstabilized liquid SO_3 can be utilized without problem as long as moisture is excluded and it is maintained at $\sim$27–32°C. Stabilized liquid SO_3 has an advantage in that should the liquid freeze (16.8°C) in the absence of moisture, the SO_3 remains in the γ-isomer form and is readily remeltable (Table 3). Freezing of unstabilized liquid SO_3 results in higher melting β- and α-forms, with a somewhat dangerous pressure release on melting. Commercial stabilizers include B_2O_3 and B_2O_3 esters, borontrifluoride, CCl_4, methane sulfonic acid, methane sulfonyl chloride, and phosphorous oxychloride (16). Gaseous SO_3 can also be obtained by stripping 70% oleum (70%SO_3:30%H_2SO_4) or by utilizing SO_3 converter gas (6–8% SO_3) from H_2SO_4 production. As of 2005, it appears that DuPont was the sole U.S. supplier of liquid SO_3.

Sulfur trioxide is an extremely strong electrophile that enters into transient complexes or irreversible reactions with organic oxygenates, eg, aldehydes, ketones, carboxylates, esters, and ethers; nitro compounds; phosphates; sulfonates; and sulfates. For example, acetone appears to form a complex with SO_3 at −20°C in inert solvent, but also readily reacts with SO_3–dioxane complex to afford mono- and disulfonates (17). Sulfonic acids are reactive with SO_3 to form mixtures of sulfonic acids, pyrosulfonic acids, and sulfonic anhydrides (17). The presence of significant amounts of pyrosulfonic acids in the initial acid product during commercial sulfonation of linear alkylbenzenes is a practical example. The SO_3 "tied-up" in these pyrosulfonates functions as sulfonation reagent for unreacted LAB in the subsequent thermal digestion of acid.

The ability of SO_3 to form complexes with even extremely weak lewis bases has practical utility for the mitigation of SO_3 reactivity. The reactivity of such complexes is inversely proportional to their stability, and consequently they can be selected for a wide variety of conditions. Example complexation agents include pyridine, trimethylamine, 1,4-dioxane, dimethylformamide (dmf), and triethyl phosphate (17). Whereas moderating SO_3 reactivity by adducting agents is generally beneficial, the agents add cost and may contribute to odor and possible toxicity problems in derived products. Cellulosic material has been sulfated with SO_3–trimethylamine adduct in aqueous media at 0–5°C (18). Sulfur trioxide–triethyl phosphate has been used to sulfonate alkenes to the corresponding alkene sulfonate (19). Sulfur trioxide–pyridine adduct sulfates oleyl alcohol with no attack of the double bond (20). In addition to the use of complexation agents, the extreme and violent reactivity of liquid SO_3 can be moderated by using (*1*) liquid solvents, eg, low boiling saturated hydrocarbons, liquid SO_2, or halogenated hydrocarbons (methylene chloride or ethylene dichloride); (*2*) H_2SO_4 acid heel, ie, *in situ* oleum, gaseous SO_3 sulfonation system; (*3*) vaporization of liquid SO_3; and (*4*) vaporization of liquid SO_3 and dilution with dry gases, eg, air, N_2, or SO_2. The latter approach has the broadest commercial applicability. It should be noted that stabilizers in liquid SO_3 can serve as catalysts that can accelerate SO_3 reactions, particularly with the halogenated solvents. A mixture of liquid-stabilized SO_3 and ethylene dichloride reportedly exploded violently after being left standing at room temperature (21). Such reactions can be substantially avoided by distilling SO_3 from its stabilizer before mixing with such solvents, and using such mixtures immediately thereafter. Liquid sulfur trioxide secured from chemical supply houses undoubtedly contains stabilizers.

Table 4 summarizes frequently used sulfuric acid, oleum, and liquid SO_3 sulfonating agents and their properties. Oleum, chlorosulfonic acid, and liquid SO_3 sulfonation reagents are all classified as hazardous and toxic chemicals, mandating special handling, storage, and usage procedures. These procedures are readily available from respective suppliers. Sulfur trioxide vapors released from the handling or spillage of oleum or liquid SO_3 react rapidly with atmopheric moisture to produce a sulfuric acid fog or mist.

A comparison of differences in the use of H_2SO_4–oleum versus gaseous SO_3 sulfonating agents is presented in Table 5. A listing of frequently used indirect means of introducing the sulfonate group through other reactions is assembled in Table 6. Comparative heats of sulfonation and sulfation reactions are listed in Table 7 for significant anionic products using SO_3 and oleum reagents (16).

5. Sulfonation

All sulfonation is concerned with generating a carbon–sulfur(VI) bond (34) in the most controlled manner possible using some form of the sulfur trioxide moiety. The sulfonation of aromatic compounds, eg, dodecylbenzene, olefins, eg, 1-hexadecene, and esters, eg, methyl hexadecanoate, are all examples of important commercial processes. Sulfonation can be carried out in a number of ways using the reagents listed in Table 2. Sulfur trioxide is a much more reactive sulfonating reagent than any of its derivatives (see Tables 2 and 4) or adducts. Care should be taken with all sulfonating reagents owing to the general exothermic nature of the reaction. For example, $\Delta H = -170\,\text{kJ/mol}$ ($-40.6\,\text{kcal/mol}$) for dodecylbenzene sulfonic acid (see Table 7).

5.1. Aromatic Compounds. The variety of sulfonation reagents available makes possible the conversion of a wide range of aromatics into sulfonic acids. The postulated mechanisms of aromatic sulfonation with respect to various sulfonating reagents, including SO_3, H_2SO_4, oleum, and chlorosulfonic acid, have been reviewed (35). The accepted general mechanism (35–38) for the reaction of an aromatic compound with sulfur trioxide involves an activated intermediate as shown in equation 1.

$$R - C_6H_5 + SO_3 \longrightarrow [R - C_6H_5SO_3]^* \longrightarrow R - C_6H_4SO_3H \qquad (1)$$

The intermediate is believed to form through a π-complex, which collapses into a σ-complex, which then rearomatizes upon proton removal from the sp^3 carbon. This proton loss is followed by addition of a proton to the oxygen of the aromatic sulfonate. Key side reactions of concern during the sulfonation of aromatic compounds include sulfone formation and sulfonic acid anhydride formation. For example, direct sulfonation of benzene with 1.3 molar equivalents of SO_3 at 25°C affords a product mixture with a sulfone to sulfonic acid ratio of 0.6 (35).

Benzene, Toluene, Xylenes, and other "Simple" Aromatic Hydrocarbons. The sulfonation of simple aromatic compounds, eg, benzene, toluene, *o*-xylene, etc, is commonly practiced using H_2SO_4 or oleum. Three key factors that affect the ability to convert aromatic hydrocarbons to sulfonic acids with these reagents include (*1*) the reactivity of the aromatic compound; (*2*) water-generation and limiting converion: the so-called π factor; and (*3*) kinetic versus mass transfer control of reaction rates. The study of the sulfonation kinetics of simple aromatics with H_2SO_4 or oleum is very much complicated by the hetergoeneous nature of the reaction system (39), and therefore the relative rates of aromatic sulfonation under industrially relevant conditions is not readily gleaned from the chemical literature. The decending relative rates of homogeneous H_2SO_4 sulfonation of simple aromatic compounds in nitrobenzene have been reported as: *o*-xylene (*17.8*), *m*-xylene (*7.5*), toluene (*5.1*), ethylbenzene (*4.8*), cumene (*3.4*), and benzene (*1.0*) (17). Some data has been published on solvent-free H_2SO_4 sulfonation of aromatics under homogenous conditions (aromatic concentration below solubility limits), where relative differences in reaction rates are much greater (40,41). For reactions in concentrated sulfuric acid, the rates of sulfonation decrease as water concentration builds-up (inversely proportional to the square of water concentration). It has been reported that under homogeneous pseudo-first-order reaction conditions, the relative rate of *o*-xylene sulfonation at 86.1% H_2SO_4 concentration is 18,500 times faster than at 70.9% H_2SO_4 concentration (41). Sulfonation conversion ceases when the sulfuric acid strength (% H_2SO_4) reaches a certain level: the π factor. This level is characteristic of the aromatic compound being sulfonated. In industrial processes, overcoming the limitations imposed by the formation of water during sulfuric acid sulfonation of simple aromatics is commonly achieved by azeotropic removal of water from the reaction system.

Salts of sulfonated toluene, xylene, and cumene are important industrially as hydrotropes or coupling agents in the manufacture of liquid cleaners and other surfactant compositions. They also serve as crisping agents in drum and spray drying operations. Toluene sulfonation (42) yields 79% *para*-, 13% *ortho*-, and 8% *meta*-toluene sulfonic acid at 100°C. Isomer ratios change with temperature owing to the Jacobsen rearrangement.

Dyes, Dye Intermediates, and Naphthalene. Several thousand different synthetic dyes are known, having a total worldwide consumption of 1.2 million metric tons/year as of 2003 (9) (see DYES AND DYE INTERMEDIATES). Many dyes contain some form of sulfonate as $-SO_3H$, $-SO_3Na$, or $-SO_2NH_2$. Acid dyes, direct dyes, solvent dyes, basic dyes, disperse dyes, fiber-reactive dyes, and vat dyes can have one or more sulfonic acid groups incorporated into their molecular structure. The raw materials used for the manufacture of dyes are mainly aromatic hydrocarbons and include naphthalene, anthracene, pyrene, phenol, pyridine, and carbazole. Key dye intermediates obtained by sulfonation include benzene 1,3-disulfonic acid, anthraquinone-1-sulfonic acid, *m*-nitrobenzenesulfonic acid, and many other compounds (see DYES AND DYE INTERMEDIATES). A review of sulfonated vat dyes was published in 2002 (43).

The manufacture of sulfonated naphthalene compositions represented 23% (25,000 metric ton/year) of the total U.S. consumption of napthalene in 2003. In Western Europe, the sulfonated napthalene accounted for 35% of all naphthalene consumption in the same year (13). Sulfonated naphthalene usage is divided between alkyl naphthalene sulfonates for industrial applications as nondetergent wetting agents (~10% of U.S. usage in 2003) and naphthalene sulfonate-formaldehyde condensates for use as concrete additives (superplasticizers), dispersants for pesticides, fluidizers for gypsum wallboard manufacture, intermediates in dye manufacture, and synthetic tanning agents (~90% of U.S. usage in 2003) (13).

Alkylated Aromatics. The world's largest volume synthetic surfactant is linear alkylbenzene sulfonate (LAS), with an estimated world production of 3 million metric tons in 2001 (44). LAS is derived from the sulfonation of linear alkylbenzene (LAB). Detergent sulfonates use LAB in the 236–262 molecular weight range, having a C_{11}–C_{13} alkyl group. The favored industrial sulfonation route utilizes SO_3–air mixtures in falling film reactors, which provides products that are 97–98% surfactant active and of excellent color. The simplest routes for sulfonation of LAB use 100% sulfuric acid. The by-product is water, which dilutes the sulfuric acid and establishes an equilibrium so that $< 100\%$ yield of sulfonic acid is obtained. A large excess of sulfuric acid is therefore required. Oleum (10–25% sulfur trioxide in sulfuric acid) may be used instead of sulfuric acid, reducing somewhat the large amount of sulfate in neutralized product. In all these processes, sulfur trioxide is the sulfonating agent and the primary product is the *para*-alkylbenzene sulfonic acid, which may be neutralized using any of a variety of bases. Examples include sodium, calcium, magnesium, ammonia, isopropylamine, or triethanolamine. Sodium is the most common salt produced because of its cost and performance. Neutralized slurries can show a pH drift if sulfonic anhydrides and pyrosulfonic acids not destroyed during processing. Treatment using a small amount of water eliminates this problem, improves the yield of sulfonic acid active, and also helps to prevent darkening of the sulfonic acid.

LAS production in 2002 was estimated at 320,000 metric ton/year in North America and 445,000 metric ton/year in Western Europe (1). While LAS remains the largest volume surfactant globabally as of 2005, use of LAS in North American laundry detergents is exceeded by alcohol ethoxylate sulfates (AES), which are favored somewhat over LAS in heavy duty liquids. In fact, the consumption of AES in the United States and Canada exceeded that of LAS by $\sim$50% in 2003 (7).

5.2. Sulfitation and Bisulfitation of Unsaturated Hydrocarbons. Sulfites and bisulfites react with compounds such as olefins, epoxides, aldehydes, ketones, alkynes, aziridines, and episulfides to give aliphatic sulfonates or hydroxysulfonates. Linear alkane sulfonates are produced by the free-radical addition of sodium bisulfite to α-olefins; 1,2-disulfonates are also products of this reaction. Process conditions can be varied so as to control the level of mono versus disulfonation, with disulfonate contents ranging from $<10\%$ to 70% (45).

5.3. Sulfosuccinates and Sulfosuccinamates. The principal sulfonating reagent in these cases is the bisulfite molecule, which readily attacks electron-deficient carbon centers. The starting materials are all electron-deficient double bonds, made so by their attachment to two vinylically situated electron-withdrawing groups; ie, carboxyl groups or their ester–amide derivatives, eg, maleic acid, fumaric acid, etc. Often the mono- or diester–diamide derivatives are made to react with the aqueous bisulfite giving the resulting sulfonated product. Variations in the choice of starting material can give a broad spectrum of products of widely varying chemical and physical properties. Industrial sulfosuccinate surfactants are commonly derived from maleic anhydride (46). Monoalkylsulfosuccinates are readily prepared by the reaction of one mole of alcohol with maleic anhydride, followed by sulfitation and neutralization. Dialkylsulfosuccinates are prepared by comparable chemistry, but with the use of 2 mol of alcohol for every mole of maleic anhydride. Dialkylsulfosucinnates are well established as exceptional wetting agents.

5.4. Unsaturated Hydrocarbons. The reaction of long-chain, ie, C_{12}–C_{18}, α-olefins with strong sulfonating agents leads to surface-active materials (see SURFACTANTS). The overall product of sulfonation, termed α-olefin sulfonate (AOS), is a mixture of isomeric alkenesulfonates (65–70%) and hydroxyalkanesulfonates (20–25%), along with small amounts of disulfonated products (7–10%) (47,48). AOS manufacture is typically comprised of the steps of sulfonation, digestion, neutralization, and hydrolysis. Chemical pathways that lead to individual components within these mixtures has been described (49). The composition of the final product varies as a result of manufacturing conditions, and it is possible to exercise a limited amount of control over the final product mixture.

The exothermic (−210 kJ/mol, −50.2 kcal/mol) nature of the SO_3–olefin reaction makes a neat process impractical, and continuous thin-film sulfonators with dilute SO_3 in dry air are typically used to manufacture AOS. Batch processes employ SO_3 complexed with a Lewis base and/or a solvent system, eg, liquid SO_2. Sulfonation of α-olefins may also be carried out with chlorosulfonic acid.

The initial SO_3 sulfonation reaction involves the formation of a carbon–sulfur bond at the terminal carbon of the olefin in accordance with Markovnikov's rule to make the four-membered β-sultone ring (50,51), which is believed to occur through a concerted $\pi 2s + \pi 2s$ cyclo- addition mechanism (52). β-Sultone can further react with more SO_3 to form a cyclic pyrosulfonate ester. Other names include pyrosultone, carbyl sulfate, or cyclic sulfonate–sulfate anhydride (53–55). The pyrosultone is metastable and can decompose upon aging to alkene sulfonic acid with the release of SO_3. This SO_3 is free to react with any remaining olefin or with the double bond of alkenesulfonic acids to form disulfonic acids. The decomposition of pyrosultones, as well as general equilibration of the crude product mixture, moves the process into a stage often referred to as digestion or conditioning. In the digestion phase, highly strained β-sultones isomerize to a mixture of *n*-alkenesulfonic acids, as well as five- or six-membered ring structures referred to as γ-sultones or δ-sulfones, respectively. If digestion is not carried out, the neutralized product contains a high proportion of 2-hydroxyalkanesulfonate, which is very insoluble. Approximate digestion conditions for β-sultone removal are from 30 to 50°C for 1–30 min.

Extended digestion increases the ratio of δ- to γ-sultone, as the six-membered ring is thermally favored, and also results in very gradual conversion of alkenesulfonic acids to δ-sultone. High temperature digestion (∼150°C), results in oligomerization of the acid to afford complex mixtures of saturated alkane sulfonates (56).

Variation of conditions for hydrolysis of the intermediate sultone mixture can modify the ratio of alkenesulfonate to *n*-hydroxyalkanesulfonate, distribution of alkenesulfonate positional isomers, and completeness of conversion. Caustic hydrolysis using a slight stoichiometric excess of base is employed to ensure alkaline conditions throughout the hydrolysis phase of AOS production. AOS prepared from α-olefins in the C_{12}–C_{18} range are most suitable for detergent applications. Generally, alkenesulfonates show better detergency and foaming than *n*-hydroxyalkanesulfonates. Sulfonates of branched and internal olefins are poorer detergents but have good wetting properties.

Historically, the sulfonation of internal olefins had been regarded as a difficult process, with only 80 or 90% yields expected. However, it is now recognized that there are substantial differences in the decomposition pathways of β-sultones derived from internal olefin versus α-olefin. In particular, internal β-sultones are prone to desulfonation reactions that result in regeneration of olefins and severe color formation. Therefore, high conversion of internal olefins to sulfonated product requires that acid digestion be avoided and that neutralization be conducted immediately following sulfonation (57).

5.5. Sulfoxidation and Sulfochlorination of Paraffins. Sulfoxidation and chlorosulfonation are free-radical processes, typically driven by ultraviolet (uv) irradiation, that are used for the production of secondary alkane sulfonates. It is estimated that ∼ 250,000 metric tons per year are currently produced, mainly in Europe as well as some production in Russia and Japan. The chlorosulfonation process was first used in Germany starting in 1940 to produce synthetic detergents. Since the sulfoxidation is found to be more economical, it is currently used for ∼ 75% of the world's total secondary alkane sulfonate production.

The sulfoxidation of paraffins is made possible by the use of free-radical chemistry with sulfur dioxide and oxygen (58,59), whereas sulfochlorination of paraffins entails the use of a mixture of sulfur dioxide and chlorine (known as the Reed reaction) (60). While uv irradiation is typically used, free radicals can be generated in any number of ways. The processes produce random substitution and significant disulfonation (61). One of the primary problems associated with generating the free radicals by uv irradiation is that colored materials are deposited on the light source, impairing the illumination and retarding the process (62). The C_{14-17} paraffin sulfonates, sometimes referred to as secondary alkanesulfonates (SAS), are quite water soluble surfactants and are primarily utilized in liquid detergents and concentrates.

A recent report describes the use of sulfuryl chloride for the photosulfochlorination of paraffins (63). Another publication reviews the synthesis and properties of dodecane sulfonates (64). The use of this type of process technology has recently been applied to the photochemical sulfoxidation and chlorosulfonation of saturated fatty methyl esters to produce a new type of surfactant based on renewable sources of feedstock (65–69).

5.6. Fatty Acid Esters. Fatty acid ester sulfonates are manufactured by reaction of the corresponding hydrogenated ester and a strong sulfonating agent, typically sulfur trioxide, in order to sulfonate on the α-position of the ester. Huish Company's recent installion of a large sulfonation plant in Houston, Tex. includes the manufacture of methyl ester sulfonates (MES), primarily for use in powdered laundry detergent, and resulted in an increase in MES consumption of ∼16,000 metric tons in the United States from 2000 to 2003 (7). Because of the relatively low cost of methanol and favorable product characteristics, the vast majority of patent literature is focused on MES rather than higher alkyl ester sulfonates. The acid form of MES can be transesterified with alcohols, diols, and polyols (70) to afford a vast array of compositions. Unlike detergent alkyl benzene sulfonates, which are commonly produced, transported, and stored in sulfonic acid form, MES is neutralized, typically as the sodium salt.

The manufacture of MES typically comprises five distinct processing stages; sulfonation, digestion, reesterification, neutralization, and bleaching, all of which are ammenable to continous processing. The order of processing for the neutralization and bleaching stages can be reversed. The first stage is sulfonation, usually with dilute SO_3 gas in air. The initial adduct of SO_3 with methyl ester is believed to be a mixed anhydride, which can be thought of as an insertion product of SO_3 into the methyl ester group. This intermediate is highly reactive toward a second mole of SO_3, possibly via a $2 + 2$ cycloaddition of SO_3 to the hydrogen-bonded cyclic enol form of the mixed anhydride. Such an addition product is believed to undergo subsequent rearrangement to α-sulfonated mixed anhydride (71). Thus, a relatively stable intermediate that is formally a 2:1 adduct of SO_3 with methyl ester is obtained.

High quality methyl ester feedstocks typically require approximately 1.1–1.2 mol equivalents of SO_3 to achieve full α-sulfo conversion, and the acid product obtained by initial contact of SO_3 with methyl ester is a mixture of 2:1 adduct and unreacted methyl ester. The second stage, then, is to convert the unreacted methyl esters in this mixture to α-sulfonated product by utilizing the “stored” SO_3 in the 2:1 adduct. This stage entails thermal digestion of the sulfonation acid, with an exemplary time and temperature condition of 90°C for 30 min (72). At the end of this stage, the acid product will contain residual mixed-anhydride species that, if subjected to aqueous neutralization conditions, would hydrolyze to afford α-sulfonated fatty acid salts (commonly referred to as disalt). Sodium disalt surfactants have poorer solubility than MES and are commonly viewed as having lower detergency than the corresponding MES. Therefore, the acid is typically treated with methanol (third stage, reesterification) to convert the α-sulfonated mixed anhydrides into α-sulfonated methyl esters prior to neutralization (73).

The sulfonation and subsequent thermal digestion of methyl esters results in severe color formation. Typical methyl ester sulfonate acid may have Klett colors of several thousand. Isolated color bodies have been analyzed as conjugated polyenes with pendent vinyllic sulfonate groups (74). A number of analytical metrics for methyl ester feedstock quality have been reported as important in minimizing the severity of color formation, including low iodine values (<0.5, more preferably <0.2) (75), low hydroxyl values (76), and low carrotinoid content (77). Trace levels of oxo compounds have been reported to be particularly detrimental to feedstock quality (74). The addition of certain salts such as fine particulate Na_2SO_4 to the methyl ester stream during sufonation is known to significantly reduce color body formation (78). However, the incorporation of insoluble salts into methyl ester feedstock is problematic for conventional falling film reactor technology. Lion has reported continuous sulfonation of methyl esters in the presence of particulate sulfate salts using a highly turbulent “psuedo-film” reactor (79).

Even high quality methyl esters that are sulfonated in the presence of a color inhibitor afford digested acids of color that is unacceptably dark for most applications. Therefore, some mechanism of removing color, usually bleaching, is required for MES products to have commercial utility in consumer product formulations. A no-bleach manufacturing process for removing the color bodies from potassium MES by repeated recrystallization has been reported (80). Bleaching can be accomplished either prior to neutralization, typically with H_2O_2 in the presence of excess methanol, or after neutralization with H_2O_2 or NaClO. Through careful control of methyl ester quality parameters and the use of modern sulfonation, neutralization, and bleaching technologies, MES products of excellent color can be manufactured.

5.7. Lignin. Lignosulfonates are complex polymeric materials obtained as by-products of wood pulping where lignin is treated with sulfite reagents under various conditions. Only a fraction of the potentially available lignosulfonate is recovered owing to limited markets, low market prices, and the cost of refining and further upgrading of this by-product. Lignin by-products had historically been discharged into waterways. However, pollution regulations now require recovery and reprocessing of these materials. Lignin polymers contain substantial amounts of guaiacyl units, followed by *p*-hydroxyphenyl and syringyl units. Two principal wood pulping processes are utilized: the sulfite process and the kraft process. Sulfonation of lignin occurs mainly on the substituted phenyl—propene precursors at the α-carbon next to the aromatic ring.

Marketable lignosulfonates include ammonium, aluminum, calcium, chrome, ferrochrome, magnesium, potassium, sodium, and amine salts, and various combinations. Consumption of lignosulfonates may be divided into the following uses: animal feed pellets (13%), concrete additives (45%), road dust control (11%), oil-well drilling muds (4%), pesticide dispersant (5%), and other uses (22%) (11). Vanillin (3-methoxy-4-hydroxybenzaldehyde) is manufactured almost exclusively from lignosulfonate raw materials (81,82).

Several reviews are available covering lignosulfonate production, properties and uses (83,84). Recent developments include a process patent covering the steps of methylating a lignin compound with formaldehyde, followed by sulfonation using sulfite or bisulfite reagent to produce a dye dispersant (85). Another patent discloses a method for the fractionation of sulfite cooking liquor divised to enrich the lignosulfonate fraction (86). A process patent was issued covering the nitric acid oxidation of lignosulfonates (87).

The growing demand for oil in the People's Republic of China has spawned a signficant effort to develop and apply chemical surfactant tertiary oil recovery methods in efforts to sustain and enhance oil production. Several reports and patents have been issued for utilizing lignosulfonates as sacrificial agents, and for chemical treatments of lignosulfonates that improve surface active properties and enable use as primary surfactants in surfactant oil recovery systems (88–96). Lignosulfonate modifications included a high temperature alkylation with halogenated paraffin (89) and reaction with a long-chain amide (90).

5.8. Petroleum and Related Feedstocks. Oil soluble sulfonates represent a class of sulfonates having equivalent weights of at least 385, and more generally between 400 and 750. Such sulfonates have found a great number of industrial applications since petroleum refining first involved treatment with oleum, producing petroleum sulfonates as by-products. These applications include lubricant additives for high performance engines, as emulsifiers, flotation agents, corrosion inhibitors, and for use in enhanced oil recovery. As the demand for petroleum sulfonates increased, first-intent synthetic oil soluble sulfonates were developed. However, in many applications, these synthetic alternatives are not direct substitutes.

Global technological changes and commensurate economic benefits in petroleum refining, together with advances in sulfonation systems over the past two decades have brought about gradual changes in the oil soluble sulfonate markets and product offerings. Details for the production of petroleum sulfonates has been previously reviewed (97). The U.S. production of petroleum sulfonates has been gradually declining, but the closing of Shell's very large Martinez, CA oleum-based petroleum sulfonate plant in 2003 brought about a major shift to synthetic-based oil soluble sulfonates. The only remaining U.S. provider of petroleum sulfonates is Pennrico-Morco with an estimated annual production of ~8000 metric tons. Chemtura Corp. (Great Lakes-Crompton merger) supplies some petroleum sulfonates from their European operations. These petroleum sulfonates are marketed primarily to metal-working and corrosion inhibitor specialty manufacturers.

Sulfonation of petroleum feedstocks that are comprised of complex multiple aromatic and saturated ring structures are prone to produce undesirable oil-insoluble polysulfonates that must be separated as "sludge-spent acid" for ulitimate disposal. This issue occurs using oleum or SO_3, although the latter produces less polysulfonates than oleum processes. The manufactures of lube additives have mostly switched to synthetic long chain alkylated aromatic feedstocks using continuous SO_3 sulfonation systems, thereby avoiding polysulfonate formation and sludge disposal problems. Note that C_{12} alkylbenzene sulfonic acid, which when neutralized with common bases such as NaOH affords water soluble sulfonates, can be converted to oil soluble sulfonate by neutralization with selected amines (eg, isopropylamine) or $Ca(OH)_2$.

Sulfonates for Enhanced Oil Recovery. The use of hydrocarbon sulfonates for reducing the capillary forces in porous media containing crude oil and water phases was known as far back as 1927–1931 (98,99). Interfacial tensions between 10^{-9} and 10^{-11}N/m or less were established as necessary for the mobilization and recovery of crude oil (100,101). Oil recovery research and development was conducted by major oil company research departments utilizing petroleum sulfonates during the 1960–1975 period, since over two-thirds of the original oil is left unrecovered in a typical reservoir after primary and secondary water flooding. The U.S. Department of Energy (DOE) stimulated enhanced oil recovery pilot field tests and ultimately field expansion demonstrations by providing government incentives during the late 1970s and well into the 1980s, utilizing a broad spectrum of recovery processes. The U.S. government was concerned about national security since at that time the United States was able to produce only 60% of the nation's crude oil requirements. Micellar–polymer (MP) chemical enhanced oil recovery systems were demonstrated to have the greatest potential of all of the recovery systems under study and equivalent oil recovery for mahogany and first-intent petroleum sulfonates has been shown (102). Many somewhat different sulfonate, ie, slug, formulations, slug sizes (pore volumes), and recovery design systems were employed. Most of these field tests were deemed technically successful, but uneconomical based on prevailing oil market prices (102).

Stepan Co. developed its falling film continuous SO_3 sulfonation technology to produce petroleum sulfonates from available oil refinery feedstocks. The company built a large plant to produce and supply significant quantities of these oil soluble sulfonates to about 30 micellar–polymer field tests and expansions conducted in the United States, Europe, and Japan during the 1977–1985 period. However, with continuing and prevailing low crude oil prices, this plant was converted to produce lube sulfonates and traditional sulfonates. Since crude oil prices generally were very low (\$10–15/barrel), there was little incentive to conduct further field studies. The results of some 50 field studies for polymer, alkali, and micellar flooding methods were tabulated and assessed (102,103). One of the largest and technically successful micellar polymer field expansion operations was conducted by Chevron at the Glenn Pool Oklahoma Reservoir, where one-third of the remaining oil was recovered totaling $>$ 1.14 million barrels of crude oil (104).

Typical micellar–polymer processes utilized 3–5% active petroleum sulfonate "slugs". To conduct such a flood requires a good geological characterization of the reservoir, laboratory develoment of a suitably tailored surfactant "slug" and polymer fluids, and conducting laboratory core floods using reservoir sandstone coring that is recovered by drilling. Together, these requiements demand perhaps at least 2 years of technical support and preparatory work. Injector wells must be drilled, and construction of fluids tankage, pumping and field piping facilities must be simultaniously completed. Such projects require significant up-front investment, while ultimate crude oil production lags and continues generally over several years. Thus, these are high risk projects.

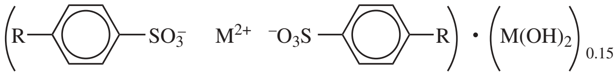
The high costs associated with the micellar/polymer process has refocused attention on a much lower cost alkali, surfactant, and polymer process referred to as ASP. The ASP surfactant slug generally contains $\sim$ 0.8 wt% alkali as Na_2CO_3, $NaHCO_3$, $NaSiO_3$, or NaOH and $\sim$ 0.1 wt% active surfactant, which is followed by $\sim$ 1000 ppm polymer. A field test engineered by Surtek (Denver, Col.) demonstrated a 20% recovery of original in-place oil in a Wyoming reservoir (105).

Pertinent recent developments in enhanced surfactant flooding over the past decade have appeared in the technical literature (102–126). Several review articles have been published (102,106,108–111). A substantial number of published reports on oil recovery methods focus on the lower cost ASP process (102,107,112–118). The ASP field test run in the Cambride-Mennelusa, Wyoming reservoir provided good oil recovery (119). Because the Peoples Republic of China has limited oil reserves and a rapidly growing demand for oil supply, the Chinese government has mandated and instituted a major effort to futher develop and utilize the ASP process in their depleted oil reservoirs. Several Chinese reports cover results of their successful ASP field pilot tests (109,113,120). The Chinese programs are based on internal development and manufacturing of the required chemicals, and include SO_3 film sulfonation to produce oil soluble sulfonates (121,122). Problems with demulsfication of ASP produced oil has been reported as a technology hurdle (118). Because of their successes in several ASP pilot field projects, the Chinese have very recently (September 2005) decided to proceed with ASP on a field-wide basis.

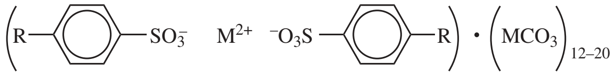
Most oil recovery studies have shown better performance with petroleum sulfonates or synthetic branched-chain alkyl aromatic-derived oil soluble sulfonates. ASP interest has been increasing elsewhere towards utilizing this type of process in the United States (119), Canada (103,111,123), in the North Sea (124), and Saudi Arabia (115). The U.S. budgetory constrainsts have resulted in minimal DOE support efforts, thus leaving EOR options to free market forces. Impediments to expoiting ASP technology in the United States include: (*1*) the need for sufficiently high and relatively stable crude oil prices to reduce economic risk; (*2*) reservoir heterogeneity; and (*3*) the practice by major oil companies, with leading reservoir engineering and financial resources, of selling off oil reservoir leases to independent oil producers during water flood stages. These independent producers have limited technological and financial support relative to that required to undertake ASP projects. Currently, firms such as Surtek are providing technological support. Surtek has designed and handled successful ASP field projects in the United States and in China. Thus the potential exists for broad implementation of the ASP process that could contribute significantly to improving U.S. crude oil production, which is currently down to only $\sim$ 50% of the nation's needs. A significant market for effective oil soluble sulfonates could devlop to support such an effort. In addition, an article published in 2000 cites the importance of and need for oil soluble sulfonates for extracting oil from the Athabasca Oil Sands in Canada (114).

A U.S. patent was recently issued relating to a new sulfonate composition of matter for the ASP process (117). Chevron filed an international patent on an oil recovery process based on α-olefin alkylated sulfonates (125) and another on branched *o*-xylene based alkylated sulfonates (126).

Sulfonates for Lube Additives. Most oil soluble sulfonates used as lube additives are based on calcium or magnesium salts. These salts can be produced by direct neutralization of the sulfonic acid with $Ca(OH)_2$ or $Mg(OH)_2$. Neutral or low base calcium and magnesium oil-soluble sulfonates are generally used as components in lubricants as dispersants and detergents to suspend oil-degradation products (sludge and carbon), and to help keep engine parts clean. Over-based or high alkalinity calcium and magnesium oil-soluble sulfonates are added to the lubricant formulation to neutralize the organic acids formed in the hot engine environment to prevent corrosion from acid attack. Low (**1**) and high (**2**) base lube sulfonates, where M is Ca or Mg, are typified as follows:



(**1**)



(**2**)

Most lube sulfonates are produced by direct neutralization of the sulfonic acid using the alkaline-earth oxide or hydroxide and a selected alcohol, often aided by a relatively low boiling hydrocarbon solvent. High base lube sulfonates are usually produced from the low base sulfonate by direct carbonation of excess alkaline-earth oxide and CO_2 addition. A carbonation promoter is generally used to facilitate the process. The alkalinity of a lube sulfonate is expressed as titratable base number (TBN) equivalent to milligrams of KOH per gram of sample. High base sulfonates generally have alkalinities ranging from 100 to 400 TBN, representing 12.5–50 wt % as $CaCO_3$ typically suspended in sulfonate and oil. Such high TBN sulfonates are carefully filtered to remove particulates and give optically clear products. These products suspend a substantial amount of $CaCO_3$ (rock) in a perfectly clear oil-based stable microemulsion.

The world's major producers of lube oil sulfonates are Lubrizol (40% of market), Infineum (ExxonMobil-Shell joint venture)(26%), and Ethyl (10%). Most lube sulfonates are based on high molecular weight synthetic alkylated aromatic feedstocks. Sulfonation of these feedstocks are generally conducted using high dilution, high velocity SO_3 continuous systems, such as the Chemithon jet-impact reactor or the falling film process. ExxonMobil utilizes low temperature SO_3 sulfonation with SO_2 solvent. Chevron and Ethyl produce their own high molecular weight linear alkylbenzene alkylates. ExxonMobil reportedly produces a polypropylene high molecular weight alkyaromatic alkylate. The major suppliers of combustion engine lubricants have developed very sophisticated proprietary and complex technology geared to meet very stringent performance specifications and tests. Such development is expensive and is supported by very specialized engine testing laboratories and technologists.

Recent Developments in Lube Sulfonates. A number of publications and patents have appeared in the technical literature (127–134). A review of lubricant additives was published in 2003 (128). A paper was recently published on corrosion prevention using petroleum sulfonates (132), while another paper covered molecular modeling studies for overbased sulfonates (131). A Chevron patent application was published in 1996 on the use of overbased sulfonates for marine lubrication (127). A process patent was issued in Europe for making overbased calcium sulfonate detergents (129), and a Korean patent issued covering an alkaline liquid detergent composition containing magnesium alkybenzenesulfonate (130). A Chinese paper was published on the synthesis of middle (overbased) calcium alkybenzenesulfonate for cleaning additives (133). A Chinese patent was issued covering the preparation of weak basic alkylbenzenesulfonates (134).

Recent Developments in Oil Soluble Sulfonates. Several pertinent reports and patents have appeared in the technical literature over the past decade (135–145). Several of these disclosures relate to the oil recovery program underway in the Peoples Republic of China (135–137,139–141,143–145). A new process was disclosed involving the alkylation of freshly produced long chain α-olefin sulfonic acid with benzene, etc, producing linear aromatic alkylate sulfonates where the SO_3 group is attached to the linear chain (142). Improvements upon this alkylation process have also been disclosed (146). The products have potential application in the household personal care field, and for enhanced oil recovery (117,142,146). Chinese patents have been issued on methods of producing oil recovery sulfonates (136,139–141,143–145).

5.9. Sulfonated Polymers. The incorporation of sulfonates into polymeric material can occur either at the monomer stage (polymerization method) or after polymerization (polymer sulfonation method). The sulfonic acid group is strongly acidic and can therefore be used to functionalize the polymer backbone to the desired degree. Depending on the molar fraction in the polymer, as well as on the macromolecular structure, the sulfonic acid group strongly interacts with water to bring about polymer swelling or gel formation, to a point where the complete dissolution of the polymer is possible. The ability of sulfonic acids to exchange counterions has made these polymers prominent in industrial water treatment applications, such as ion-exchange resins for demineralization, membranes for reverse osmosis or Donan dialysis, separators in electrochemical cells, and selective membranes of many types. Being strongly polar, the sulfonate functionality is used in such diverse areas as textile fiber dyeability, in thickeners and flocculants, rubber modifiers, and adhesive promoters. In addition, sulfonic acid derivatives, such as sulfonyl chlorides, amides, and anhydrides, make for an even wider range of uses.

The polymerization method for incorporation of sulfonate moeities into polymers entails the use of monomers that contain sulfonic acid or sulfonate groups. These monomers may be homopolymerized or copolymerized with a variety of other monomers to afford a host of polymeric materials that can be varied in terms of molecular weight and degree of sulfonation. The simplest monomer, ethylenesulfonic acid, can be prepared by elimination from sodium hydroxyethyl sulfonate and polyphosphoric acid (147). Sodium ethylenesulfonate can be prepared by first reacting ethanol with two moles of SO_3 to afford ethionic acid ($HO_3SOCH_2CH_2SO_3H$), followed by treatment with caustic to eliminate Na_2SO_4 (148). Ethylenesulfonic acid and various neutralized salts are readily polymerized alone (29) or can be incorporated as copolymers using such monomers as acrylonitrile and methyl acrylate (149). The monomer sodium 4-styrenesulfonate is prepared by dehydrohalogenation of *p*-halogenoethylbenzene sulfonyl chloride or sulfonic acid with aqueous caustic. It has been reported that the crystalline hemihydrate of this molecule is preferred in terms of prevention of polymerization and clumping upon storage (150). The monomer can be copolymerized with a number of other monomers, including styrene (151), butadiene (152), isoprene (153), and *tert*-butyl styrene (154). For example, $\sim$2–10% by weight sodium styrenesulfonate can be copolymerized with styrene via emulsion polymerization to afford sulfonated polymers suitable for use in sealant applications (30). DuPont's Nafion resins are representative of polymeric materials that are derived from the copolymerization of tetrafluoroethylene and sulfonic acid-containing perfluorinated monomers, eg, perfluoro[2-(fluorosulfonylethoxy)propyl]vinyl ether (155,156). The acid forms of these resins function as catalysts for a wide range of chemical transformations, including electrophilic aromatic substitutions, transalkylations, and condensations (157). The resins have been widely studied in the development of membrane fuel cells, where proton-conducting membranes can be fabricated as homogeneous ionomer and as various composits (158).

The condensation polymerization of diols with sulfonated diacids, diesters, or anhydrides such as those based on ortho-, iso-, or teraphthalate can be used to prepared sulfonated polyesters that are useful as detergent and textile applications (159). Similarly, transesterfication of sulfonated diacids into poly(ethylene terephthalate) affords sulfonated polyesters that are useful as soil release agents

(160). Dimethyl sulfosuccinate is readily prepared via the reaction of dimethyl maleate with sodium metabisulfite (161). The sodium salt is readily incorporated into polyesters via condensation with diols and other diacid derivatives.

The polymer sulfonation method for the incorporation of sulfonate moeities into polymers entails the derivatization of preexisting polymers. Typically, the derivatization involves the chemical reaction of aromatic rings, unsaturation, carboxylic acids or esters, or hydroxyl groups with sulfonation, sulfoalkylation, or sulfoacylation reagents. A broad range of polymeric materials can be derivatized by these procedures, including polystyrenes, styrene-containing copolymers, aromatic polyimides, aromatic polyether ketones, unsaturated elastomers, unsaturated polyesters, and natural polymers, eg, celluloses.

Sulfonation of aromatic-containing polymers with reagents, eg, SO_3, H_2SO_4, chlorosulfonic acid, and various SO_3 complexes can be carried under homogeneous or heterogeneous conditions (162). The synthesis of poly(styrenesulfonic acid) from polystyrene is representative of the complications that can be encountered in the sulfonation of aromatic polymers, where there is potential for oxidative degradation, oversulfonation (some rings disulfonated) and crosslinking via sulfone formation (163). For sulfonations in which water solubility and maintainance of molecular weight is targeted, even trace amounts of sulfone formation can be problematic. Through the use of catalytic silver sulfate, it is possible to achieve high conversion, negligible oversulfonation or crosslinking, and maintainance of molecular weight in the sulfonation of highly dilute, finely divided polystyrene with 100% H_2SO_4 at room temperature (164). The sulfonation of polystyrene segments in hydrogenated butadiene-styrene triblock copolymers can be achieved using acetyl sulfate (also referred to as acyl sulfate, prepared by the reaction of sulfuric acid with acetic anhydride) in methylene chloride (24). The sulfonation of aromatic polyethers, eg, polyether sulfone (165) and poly(ether ketone ketone) (166), affords materials that can be fashioned into proton-conducting membranes; a substantial body of literature exists with regard to such materials as potential alternatives to Nafion-type resins.

The commercial manufacture of sulfonated poly(styrene-divinylbenzene) ion-exchange resins typically entails the batch sulfonation of cross-linked beads obtained from suspension polymerization with sulfuric acid, oleum, or chlorosulfonic acid (167). The heterogenous sulfonation of cross-linked polystyrene beads can be accomplished as a solid–gas reaction by contacting with the SO_3 headspace of oleum (162). The sulfonation of elastomers can be achieved by a number of methods, including a continuous process in which an ethylene–propylene elastomer is reacted with acetyl sulfate in an continuous extruder that eliminates the need for solvents and simplifies polymer isolation (162).

The sulfonation of maleate group-containing polyesters can be carried out via addition of sodium metabisulfite to aqueous suspension of polymer as an alternative to condensation polymerization of sulfo-containing diacids (161). Sulfonated polyesters have been shown to be useful in the preparation of water-dispersable polyurethanes (168). Waste polyterephthalate materials can be converted to water-soluble or water-dispersable soil release agents by first transesterify scrap polymer with various condensation monomers (diols, polyols, diacids, and the like), reacting the prepolymer with maleic anhydride, and sulfonating the resultant material with aqueous sodium sulfite (169).

The reaction of sulfoalkylating agents with hydroxyl-containing polymers represents an additional means by which sulfonated polymers can be prepared. Sulfoalkylated polysaccarides are prepared by treatment of starch or gum with 1,3-propane sultone or 1,4-butane sultone under aqueous alkaline conditions (28). Concrete fluidizer (superplasticizer) with water-reducing performance superior to that of commercial napthalene sulfonate superplasticizer can be prepared by the reaction of sodium 2-chloroethanesulfonate with water-soluble starch in isopropyl alcohol and aqueous NaOH (170). A 2002 published paper reviewed the preparation and properties of cellulose sulfonates (171).

6. Sulfation

Sulfation is the generation of an oxygen–sulfur(IV) bond, wherein the oxygen is attached to the carbon backbone, in the most controlled manner possible using some form of sulfur trioxide moiety (16). When sulfating alcohols, the reaction is strongly exothermic, $\Delta H = -150$ kJ/mol (-35.8 kcal/mol) (16). The mechanism for alcohol sulfation is believed to occur through a metastable pyrosulfate specie that decomposes rapidly to alkyl hydrogen pyrosulfate, $ROSO_2OSO_3H$, which subsequently reacts with a second alcohol molecule to produce an alcohol sulfate product mixture. Examples of feedstocks for such a process include alcohols, phenols, or alkenes. The latter feedstock type is sulfated with sulfuric acid but sulfonated with SO_3. The acid products of alcohol or alkene sulfation are predominantly sulfuric acid half-esters (alkyl sulfates). Unlike sulfonic acids and sulfonates, which exhibit excellent stability to hydrolysis, these alkyl sulfates are highly susceptible to hydrolysis in acidic aqueous media. Therefore, in laboratory batch neutralization of alkyl sulfates, it is preferable to add acid to aqueous caustic rather than the inverse. The thermal breakdown of alkyl sulfates under anhydrous conditions produces a mixture of products including the parent alcohol; dialkylsulfates, $ROSO_2OR$; dialkyl ether, ROR; and isomeric alcohols, and olefins (16). It has been reported that the complete thermal decomposition of primary alcohol sulfate (PAS) acid results in a mixture of PAS, alcohol, H_2SO_4, and PAS anhydride, with one-third of the original PAS conversion lost (172). High processing temperatures must be avoided and the product neutralized soon after formation. Best product is obtained at sulfation temperatures of from 35 to 50°C and neutralization within 1 min after sulfation (16).

Linear ethoxylates are used extensively as raw materials for production of ether sulfates that are formulated into detergents. The alkyl chain is usually in the C_{12}–C_{13} range having a molar ethylene oxide:alcohol ratio of anywhere from 1:1 to 7:1. Propoxylates, ethoxylates, and mixed alkoxylates of aliphatic alcohols or alkyl phenols are sulfated for use in specialty applications.

6.1. Alcohols and Alkoxylates. Alkyl and alkoxyalkyl sulfates can be produced from the corresponding alcohols or alcohol alkoxylates by reaction with a wide variety of reagents including chlorosulfonic acid, sulfur trioxide, sulfuric acid, and sulfamic acid [5329-14-6]. The products obtained from different sulfating reagents are similar in wetting time, detergency, and foam generation. Chlorosulfonic acid gives slightly better colors, but requires disposal of HCl. Sulfation using SO_3 requires controlled reaction temperatures and short residence time between sulfation and neutralization due to the instability of the acid product. Therefore, the preferred method of sulfation uses some form of continuous thin-film reactor. It has been reported that the acid decomposition rates for sulfated fatty alcohol ethoxylates are considerably slower than for sulfated fatty alcohols (172). However, an important undesirable side reaction of ethoxylated alcohol sulfation is dioxane formation, which can range from traces to hundreds or even thousands of ppm (mg/kg) depending on raw material quality and sulfation/neutralization conditions (16,173–175). Dioxane forms by the chemical cleavage of two molecules of ethylene oxide from the parent ethoxylated alcohol. Dioxane formation is favored by an excess of SO_3, high temperatures, long aging times, moisture in the feedstock, branching of alkyl chains, and longer ethylene oxide chains in the ethoxylated alcohol feedstock (16). Process conditions that have been established to minimize dioxane formation utilize a mole ratio of SO_3 to alcohol ethoxylate of 1.01–1.02:1; SO_3 in air, 3 vol % max; and the lowest temperatures possible for feedstock, reaction zone, and aging phase (16). Other examples of sulfated alcohols are mono- and difatty glyceryl ester sulfates (176–178) and fatty acid oligo(alkylene glycol) ester sulfates (179).

6.2. Fats and Oils. In 1831, Fremy reacted castor oil with sulfuric acid producing a product called "Turkey Red Oil", which was used as a textile assistant. Historically, this represented the first "sulfation-sulfonation" produced surfactant. Prior to the development of synthetic surfactants during the 1920–1940 period, fatty oils such as sperm, tallow, peanut, soybean, castor, olive, and various fish oils were reacted with sulfuric acid and subsequently neutralized with alkali to produce crude surfactants that were used for a variety of industrial applications (17,180). Such products continue to be produced in limited quantities. These crude mixtures are difficult to characterize clearly; suffice to say that the products are chiefly sulfated mixtures.

During the period of 1995–2005, several patents were issued on the preparation of sulfonated or sulfated fatty oils or fatty acids (181,182). A Japanese patent disclosed the use of SO_3 reaction with petroleum or vegetable oils (181).

6.3. Carbohydrates. Cellulose is an abundently available and replenishable raw material that has been and continues to be researched for chemical modification. Carbohydrates of any form are easily sulfated in the presence of solvent, using sulfating reagents such as SO_3–pyridine, SO_3–triethylamine, SO_3–trimethylamine, or chlorosulfonic acid–pyridine. As an example, starch is sulfated using SO_3–trimethylamine at 0–5°C in aqueous media (18). One preparation of cellulose sulfonic esters involves the reaction of sulfonyl acid chlorides with hydroxyl groups in the presence of pyridine. The reaction of $NaHSO_3$ with cellulose in aqueous solution also produces cellulose sulfate (183,184). Sulfated carbohydrate products find some use in industry as thickening agents.

6.4. Alkenes. The sulfation of low molecular weight alkenes using concentrated sulfuric acid is amenable to continuous operation. Good agitation is required and the reaction is performed at 70–80°C. Dialkyl sulfates are also formed. Longer (C_{12}–C_{18}) carbon chain alkenes yield detergent products. Order of addition, temperature, and stoichiometry are all important to this reaction. For example, the addition of 96% sulfuric acid to 1-dodecene at 0°C yields mainly dialkyl sulfate; further addition gives an 80% yield of 2-monoalkylsulfate. If the olefin is added to the acid, random isomers are produced. A patent was issued on the sulfation of mixtures of detergent-range olefins and secondary alcohols with sulfuric acid, the process utilizing a neutralization and saponification step in the presence of nonionic surfactant to effectively hydrolyze dialkysulfates (185).

7. Sulfamation

Sulfamation is the formation (186) of a nitrogen–sulfur(VI) bond by the reaction of an amine with sulfur trioxide or one of the many adduct forms of SO_3. Heating an amine with sulfamic acid is an alternative method. Practical examples of sulfamation are the artificial sweeteners sodium cyclohexylsulfamate [139-05-9] and potassium acesulfame, produced from the reaction of sulfur trioxide with cyclohexylamine and acetoacetamide, respectively (14,187) (see SWEETENERS). Sulfamic acid is prepared from urea and oleum (188). Whereas sulfamation is not widely used commercially, sulfamic acid has various applications (see SULFAMIC ACID AND SULFAMATES) (189–193).

8. Industrial Processes

A wide array of industrial processes is suitable for the manufacture of sulfated and sulfonated products. Process selection is dependent on the specific chemistry involved, choice and cost of reagents, physical properties of feedstocks and derived products, product volume requirements, operational mode (batch, continuous), quality of derived products, possible generation and disposal of by-products, and operating and equipment investment costs. Another important consideration is the location of the sulfonation plant relative to raw material suppliers, particularly for the more limited liquid SO_3 supplier's plants. On the other hand, molten sulfur used for *in situ* sulfur burning and gaseous SO_3 generation is readily available throughout the United States and worldwide. Another consideration for process selection is plant versatility in sulfonating a variety of feedstocks. While the use of modern-day continuous falling film SO_3 sulfonation–sulfation systems has significant economic and operational advantages, in many instances, eg, for smaller specialty chemical firms with small volume requirements, the use of older processes with batch equipment is still common.

The handling of highly acidic sulfonation reagents and the actual sulfonation processing conditions for the production of acidic reaction products and by-products present a number of corrosion problems that must be carefully addressed. Special stainless steel alloys or glass-lined equipment are often used, although the latter generally has poorer heat-exchange properties. All environmental regulations or restrictions must also be met. For example, in utilizing $ClSO_3H$ reagent, HCl gaseous by-product is generated requiring its recovery by adsorption or neutralization.

The viscosity of sulfonation and sulfation reaction mixtures increases with conversion, often producing very high viscosities. Figure 1 provides temperature–viscosity curves for oleum and SO_3-derived products. Sulfonation process design must accommodate such viscosities.

8.1. Sulfoxidation and Chlorosulfonation Processes. Both sulfoxidation and chlorosulfonation processes are used commercially, operate in continuous mode, and are based on using C_{14-17} paraffinic feedstocks. Several comprehensive reviews have recently been published, providing details of the free radical chemistry, process flow diagrams, compositional data, and properties of the derived products (194–196). The chlorosulfonation process utilizes O_2 and Cl_2 to first produce the paraffin sulfonyl chloride, which is subsequently saponified to produce the corresponding paraffin sulfonate salt. The sulfoxidation process uses SO_2 and O_2. Undesirable generation of polysulfonates limits the extent of sulfonation and consequently such processing involves significant recovery and recycling of large amounts of unreacted feedstocks. Both processes produce product comprised of $\sim$ 90% mono and 10% disulfonate.

8.2. Sulfamic Acid Batch Sulfation/Neutralization Process. The process for sulfating alcohols using sulfamic acid represents perhaps the simplest available process. Minimal equipment is required. The sulfation and *in situ* neutralization of alcohols, for example nonylphenol ethoxylate, is conducted using a stainless steel or glass-lined stirred kettle by first charging with the alcohol, followed by addition of a molar quantity of solid crystalline sulfamic acid, mixing and heating to 100–160°C using a N_2 atmosphere (to preserve color), followed by partial cooling and subsequent addition of appropriate solvents. The reaction produces the ammonium salt of the sulfated alcohol. This process has been largely supplanted by SO_3 processes.

8.3. Sulfitation and Bisulfitation Sulfonation Processes. Many of these reactions are conducted in a batch stirred tank system. The sulfite reagent is usually added as a concentrated aqueous solution and intimately mixed with the organic feedstock with heating, often under pressure. Because these are generally immiscible liquid or liquid–solid phase reactions, a cosolubilizer, hydrotrope, or surfactant may be added to facilitate reaction. At the larger paper pulping mills, molten sulfur is frequently burned on-site to produce SO_2 to economically make sulfurous acid and/or metal bisulfites for sulfonating lignin. Lignosulfonates are produced by the acid sulfite and the Kraft Process.

Acid Sulfite Process. In the acid sulfite process woodchips and sawdust from hardwood sources are heated under pressure with a mixture of sulfurous acid and metal sulfite, eg, calcium, magnesium, sodium, or ammonium bisulfite. Hydrolysis and sulfonation convert lignin into lignosulfonate of molecular weight between 200 and 100,000. Structures are reported to be linear at molecular weights below $\sim$ 4000, but coiled and solvated at higher molecular weights. The degree of sulfonation appears to increase with decreasing molecular weight. In processing, hydrogen, oxygen, and sulfur are added in the proportion of 4:4:1 (83). The wood material is generally digested at 125–145°C for 8–24 h during which the lignosulfonate is solubilized. The liquor is then filtered, removing the cellulosic fiber to 58% crude lignosulfonate, which may be burned for fuel value (particularly for $NH^+{}_4$ and Ca^{2+} salts) with recovery of SO_2 for recycling, or which may be upgraded, spray dried, or further chemically treated to produce chemical derivatives. Although the sulfite process has largely been displaced by the Kraft Process, most lignosulfonates are derived from the sulfite process because higher yields are obtained. A flow diagram for this complex process has been published (83). Every metric ton of chemically produced pulp generates approximately 0.5 tons of lignin liquors containing crude lignosulfonate.

Kraft Process. Wood derived from softwood sources is generally heated under pressure with a 10–20% mixture of NaOH and Na_2S for 4–6 h at ~ 165–175°C. These conditions accelerate delignification in the pulping process. In this process, kraft lignin is filtered and separated from the black liquor, subsequently suspended in aqueous media, acidified, and subjected to H_2SO_3 sulfonation at relatively high temperatures and pressures. Westvaco Corporation is reported to be the only major producer of lignosulfonate utilizing this process.

8.4. Processes for Sulfation of Fatty Alcohols with $ClSO_3H$. Lauryl alcohol can be batch sulfated by gradual addition of $ClSO_3H$ to the alcohol in a glass-lined stirred reactor over about a 2.5-h period at a temperature of 26–32°C. Gaseous HCl is expelled, aided by a slow continuous N_2 purge. A continuous $ClSO_3H$ sulfation process has been patented and used by Henkel for the production of fatty alcohol sulfates (197). Fatty alcohol and $ClSO_3H$ are continuously injected into the bottom of a 1-cm annular space within a concentric cooled vertically tapered spiral reactor. The reaction is conducted at ~ 30°C with the reaction mixture propelled upwardly owing to the HCl gas generated by the reaction. Product residence time is estimated to be 1–2 min. This process produces excellent quality products, but appears to require refrigerated cooling. The substantially lower cost for SO_3, whether liquid or *in situ* sulfur burner-generated, together with problems and additional costs associated with handling and recovering the HCl by-product, has resulted in substantial displacement of the use of $ClSO_3H$ for sulfation of fatty alcohols.

8.5. Batch Stirred Tank H_2SO_4/Oleum Aromatic Sulfonation Processes. Low molecular weight aromatic hydrocarbon, such as benzene, toluene, xylene, and isopropybenzene, are sulfonated using molar quantities of 98–100% H_2SO_4 in stirred glass-lined reactors. A condenser and Dean-Stark-type separator trap are installed on the reactor to provide for the azeotropic distillation and condensation of aromatic and water from the reaction, enabling the removal of water and the recycling of aromatic. Sulfone by-product is removed from the neutralized sulfonate by extraction/washing with aromatic that is recycled.

Polypropylene-derived branched alkyl (C_{12}) benzene (BAB) has been batch sulfonated using 60–70% oleum in liquid SO_2 solvent at temperatures of −1 to −8°C, with SO_2 serving as a self-refrigerant and viscosity reducer in the process. After sulfonation and digestion, SO_2 is stripped, recovered, and recycled (198).

Details for the nonsolvent batch oleum sulfonation process for the production of BAB sulfonic acid have been described, including an excellent critique of processing variables (199). Relatively low reaction temperatures (~ 25–30°C) are necessary in order to obtain acceptable colored sulfonate, necessitating refrigerated cooling. These processing principles apply as well to linear alkylate oleum sulfonation systems.

Table 8 provides a detailed comparative summary for branched alkylbenzene (BAB) and linear alkyl benzene (LAB) detergent alkylate sulfonation, illustrating the use of 20% oleum in both batch and continuous modes and a typical gaseous SO_3 (5% SO_3) continuous falling film sulfonation. Composition of the neat sulfonation mixtures after digestion are shown in lines 10–13. Typical free oils of ~ 1% are achievable, indicating conversion of alkylates to sulfonic acids are on the order of ~ 98.4%. It will be noted (line 11) that the neat acid mixtures for oleum sulfonations (Examples A and B) contain ~ 40% free sulfuric acid, whereas in the case of gaseous SO_3 derived neat acid (Example C) the residual H_2SO_4 was only 1.3%. The ratio of active sodium sulfonates to Na_2SO_4 on direct neutralization of these neat acid mixtures is shown on line 14. The significant amount of Na_2SO_4 by-product is acceptable as inert filler for solid detergent products, but it is unsuitable for liquid detergent concentrates.

The significant level of sulfuric acid in oleum derived detergent alkylate sulfonic acid mixtures can be reduced by the addition of water, which facilitates an aqueous phase separation and materially reduces the residual H_2SO_4. Such "spent acid", however, requires disposal or recycle back to the sulfuric acid supplier. Line 15 illustrates the improved ratio of active sodium sulfonate/Na_2SO_4 for Examples A and B.

Observation of the composition of neat acid that is derivable from the use of the continuous falling film SO_3 sulfonation process (Example C) shows significant compositional, product color, operational, and economic advantages relative to oleum processes.

It is important to point out that the reaction of sulfuric acid or oleum with organic feedstocks involves two immiscible reactants; thus, reaction is dependent entirely on significant mixing. As noted in line 7 of Table 8, in example A for the batch reaction using oleum, reaction temperature was limited to 25°C to minimize color degradation of the acid mixture. Because of this restriction and the high heat of reaction, such batch processes generally use a refrigerated cooling system.

8.6. Continuous Oleum Sulfonation Processes. To minimize the heat of reaction-heat transfer problem associated with batch processing, a continous oleum sulfonation process was developed (termed the "dominant bath" process) wherein the detergent alkylate is contacted with oleum in a stream of freshly produced sulfonic acid (20:1 recycle at ~ 55°C) in a gear pump, then through a heat exchanger in one loop, followed by a 5 min pipeline digestion system (200). This process eliminated the need for a refrigerated cooling system, a signficant improvement over batch processing. Chemithon Corp. offers such a complete sulfonation, digestion, water addition-phase separation and neutralization system (201,202). Meccaniche Moderne and Ballestra offer continuous oleum sulfonation systems based on series of stirred tanks.

8.7. Batch Stirred Tank SO_3 Sulfonation Processes. If the color of the derived sulfonate is not critical, such as in the production of oil-soluble ag-emulsifiers, a simple batch sulfonation procedure can be employed based on vaporizing liquid SO_3 (Ninol Labs, 1952) (203). Pilot Chemical Company adapted the original Morrisroe 60–70% oleum–SO_2 solvent sulfonation process (198) to utilize 92% liquid SO_3–8% liquid SO_2 mixtures, and later using 100% liquid SO_3. This cold, low viscosity sulfonation process produces excellent quality products, and reportedly has also been adapted for continuous processing as well. The derived sulfonic acid must be stripped of SO_2 solvent after completing sulfonation and digestion. Details of commercial scale batch SO_3 sulfonation have been published (204,205).

8.8. Continuous SO_3 Single-Pass Sulfonation Processes. After the commercial introduction of stabilized liquid SO_3 in 1947, it took several years of process research to develop a suitable continous SO_3 sulfonation process. One reason for the slow development was anchored in the belief and experince that sulfonate quality, including color, was best achievable at very low temperatures (eg, at 0–25°C) (206). At such low temperatures, sulfonic acid viscosities were typically very high (see Fig. 1, left side of vertical lines), thereby often necessitating the use of solvents in order to reduce viscosity. Hence, the idea that high temperature SO_3 sulfonation could achieve good results was the antithesis of the then-prevailing technology. In 1960 Stepan Company became the first to develop and commercially operate a continuous falling film SO_3 sulfonation process using its proprietary design multitubular unit for the production of alkyl benzene sulfonates, fatty alcohol sulfates, and alkylphenolethoxy sulfates (203,207). The process has subsequently been adapted to produce alcohol ethoxysulfates, α-olefin sulfonates, α-sulfo fatty methyl esters, and oil soluble sulfonates. Stepan currently (2005) utilizes this technology in about a dozen plant sites strategically located in the United States and around the world, with an estimated capacity of ~ 500,000 metric tons per year as active surfactant.

Table 9 provides a summary of major suppliers of SO_3 sulfonation process plants based on manufacturer's technical bulletins or other industry sources (16,208–211). The table provides comparative process features, eg, production plant capacities, SO_3 concentration, organic film loading rates, estimated gas velocities, and estimated gas residence times. These film reactor systems are of two basic designs: concentric annular reactors (two vertical adjacent reaction surfaces) and multitubular (vertical heat exchanger bundled tubes). Sulfonation units can be operated with SO_3 sourced in one of two ways; (*1*) receipt of liquid SO_3 that is vaporized and diluted in a dry air stream, or (*2*) on-site generation of dilute SO_3 in air via burning of molten sulfur to afford SO_2 that is then oxidized to SO_3 across a catalytic converter. All SO_3-air processes (batch and continuous) for sulfonation of alkylaromatic feedstocks are comprised of three steps: (*1*) sulfonation, (*2*) digestion, and (*3*) stabilization. The latter step generally involves the addition of about one percent water to sulfonic acid, which hydrolyzes any remaining sulfonic acid anhydrides and breaks up any residual pyroacids (16,212). As noted in Table 9, the recommended SO_3 concentration in dry air for LAB sulfonation is generally ~ 3.5–5.0%, and ~ 2.5% for sulfation of alcohol ethoxylates. The SO_3 film sulfation–sulfation process requires the organic feedstock to be a flowable liquid. In some situations, this requirement may be met through the use of warm or hot cooling media or through the co-mingling of feedstock with a second feedstock that improves flowability.

Somewhat surprisingly and in spite of basic design and dimensional differences, the different commercially available continuous reactor designs all exhibit essentially comparable features, such as organic film loading, recommended SO_3 concentrations, gas residence times, and high velocity reaction gas flow rates. Estimated reaction gas velocities are noted to range from ~ 20 to 75 m/s (55 to 167 mph) or equivalent to between gale force and category 5 hurricane-like gas velocities. None of these sulfonation–sulfation systems use any mechanical mixing. Rather, these systems rely totally on the action of high velocity reaction gas to effect mixing of the liquid feedstock film and the reaction gas. All of these sulfonation reactors provide essentially comparable cooling surfaces (0.7–1.0 m^2/kg LAB sulfonic acid/min) with the exception of the Chemithon reactor (0.23 m^2/kg min; Chemithon Corp., Seattle, Wash.). The Chemithon reactor uses the quench cooling heat exchanger at the base of the reactor to remove additional heat of reaction. Liquid residence times in falling film sulfonation reactors are estimated to be 5–20 s (16,213).

Chemithon film sulfonating–sulfating systems are of the concentric type consisting of two concentric circular reaction surfaces, each jacketed to provide for cooling media (16,208,214). Chemithon's film reactors are of a somewhat unique design in utilizing a narrower reactor wall spacing (gap) providing for essentially complete reaction to occur within their short 2-m length of tubes. The relative hot sulfonic acid (~ 75°C) is immediately quench cooled with previously produced, cooled, and recirculated acid. Organic residence time in the reactor is estimated to be only 5–15 s, but acid remains in the quench cooling loop substantially longer, although it can be varied from 2.5–4 min. Data in Table 9 for Chemithon's annular film reactor indicates that the system utilizes a very high estimated gas velocity (~75m/s, 280 km/h). Chemithon increases reactor design capacity by increasing the diameter of its concentric reactor tubes while maintaining the same gap. Derived products meet the highest industry quality standards. Feedstock is metered using calibrated and replacable metering flanges.

Meccaniche Moderne (Busto Arsizo, Italy) acquired rights to the original Allied Chemical Corp. vertical concentric reactor system (see Table 9). This firm also supplies multitubular falling film continuous SO_3 sulfonation units that are designed similarly to a heat-exchange tube bundle. These units maintain essentially the same organic loading and gas velocity as for the concentric reactor unit. The organic is fed to each tube through a mechanically calibrated slot between the internal organic distributor and the gas injector nozzle. Their unique reactor design provides for relatively easy removal of each tube, and reactor tubes can be blocked off by blank flanges at the head of the reactor, thus reducing unit capacity if desired. The lower ends of reactor tubes have double seals and packing glands designed to prevent leakage (16,209,215,216). Excellent quality products are reported.

Ballestra SpA (Milan, Italy) multitube falling film continuous SO_3 sulfonation units utilize 6-m length reaction tubes, arranged similarly to a heat-exchanger tube bundle. The reactor tubes are enlarged at the top of the unit to accommodate the organic feed system and the gas inlet nozzle which has the same inlet diameter as the remaining portion of the reactor tube. Hence, the gas inlet contributes no pressure drop to the tube. This reactor design is claimed to provide self-compensation (self-equilibration) for balancing reaction gas–liquid mol ratio in each individual tube (16,210,217). Organic feed enters into each tube through a calibrated slot and flows around the protruding gas inlet. Excellent derived product quality is reported.

Impianti per Industrie dei Tensioattivi (IIT) (Busto Arsizo, Italy) also supplies multitubular continuous falling film SO_3 sulfonation systems similar to those of Ballestra and Meccaniche Moderne. IIT has developed a unique removable organic distribution cartridge and ring system that is factory calibrated and that fits in between the SO_3 gas supply and the reactor tube assembly. The organic feed system comprises a set of plates, a spacer, and nozzels that distribute the organic feed evenly to all reaction tubes. A small volume of "barrier gas" (dry air) is bled into the organic feed system to prevent any reaction gas back-up (218). With an operational reaction gas velocity at gale-force, unit capacities range from 2000 to 40,000 MT per year to produce competitive quality derived products.

Suppliers of these sulfonation systems have indicated that so-called "nameplate" capacities can be increased by as much as 20% by increasing the SO_3 gas concentration concurrently with adjustment of the organic feed supply. This increased throughput is reportedly achieved with minimal deterioration in derived product quality.

Figure 2 provides estimated reaction profiles, including conversion, temperature, reaction gas residence time, and viscosity, for a typical SO_3 film sulfonation of linear alkylbenzene in a Ballestra multitube reactor system (16,97,211). These reaction profiles reflect how the high velocity reaction gas stream generates substantial film turbulence, expands the gas–liquid interface, provides for very rapid SO_3 adsorption and reaction, and results in a rapid increase in film temperature that maintains low film viscosity and greatly aids in effective heat removal, all occuring in a very short gas and liquid residence time. It is remarkable how such a substantial mass transfer (one part of SO_3: three parts of alkylate) can be effected with substantial heat generation and heat exchange all consumated in a controled manner and all occuring within a fraction of a second.

Inspection of these profiles show that within the first 10, 20, and 33% of reactor length, conversion of 50, 72%, and 90% occurs, respectively, with corresponding low viscosities of $\sim$ 25, 35, and 70 cps, respectively. A peak reaction temperature of $\sim$ 80°C occurs within about the first 10% of reactor length ($\sim$0.01-s gas residence time), but it generally does not appear to contribute to product color deterioration as experienced in batch sulfonation processes for temperatures $>$ 55°C (see Fig. 1) (olefin sulfonation differs from this characteristic and exhibits substantial thermal sensitivity as a consequence of the high heat of sulfonation (see Table 7) and low feedstock molecular weight). Although the bulk of LAB sulfonation reaction has been consumated within the first one-third of the reactor, thereafter the high velocity reaction gas continues to buffet, churn and move the organic film down the reactor surface, providing for essentially complete SO_3 absorption and reaction while gradually cooling the moving film. The reaction mixture exiting the reactor is comprised of sulfonic acid and small amounts of pyro-acid (sulfonic acid–SO_3 transient adduct), sulfonic acid anhydrides, unreacted alkylatate, sulfones, and H_2SO_4–oleum by-products (16,212,219).

The digestion step in LAS processing provides time for further reaction between remaining pyro-acids and oleum with unreacted alkylate, thereby contributing toward final conversion. The addition of a small amount of water completes the process by hydrolyzing any residual sulfonic acid anhydrides to sulfonic acid and by quenching the remaining H_2SO_4–oleum (16,219,220).

Organic Film and High Velocity Gas. Organic film loading of $\sim$ 0.4 kg/(h·mm) is equivalent to 0.32-mm average thickness at the point of entry, increasing to $\sim$ 1-mm average film thickness at peak temperature (where the reaction is generally ~ 50% completed), and finally to ~ 2-mm average film thickness as the acid exits the reactor (16). Falling film continuous SO_3 sulfonation systems operating at or near hurricane wind velocities generate organic film turbulance as material moves down the reactor somewhat like hurricane winds blowing over a body of water, although higher viscosity liquids are involved (Fig. 3).

Product Quality. Under ideal plant operating conditions, the quality of products derived from different continuous SO_3 film sulfonator units is unlikely to be significantly different (16). Typical LAB sulfonic acid composition is ~ 96.6% active sulfonic acid, 1.2% free oil, 1.2% H_2SO_4, and 1.0% water (16,212). Klett color for a 5% active solution is typically 15–25.

Dioxane Problem. The sulfation of ethoxylated feedstocks with SO_3 results in the production of small quantities of dioxane, a toxic by-product. The level of dioxane produced in falling film SO_3 sulfation processes can be minimized by reducing the SO_3 mole ratio, utilizing more dilute SO_3 gas, eg, 2–3% SO_3, using higher velocity gas, reducing product throughput thereby reducing peak reaction temperature, and minimizing sulfated acid residence time in equipment prior to neutralization. Utilizing the above processing techniques for the production of 2–3 mol ethoxysulfates with free oils of 2.0% on a 100% active basis, dioxane levels of <50 ppm on a 100% active basis appear attainable (16). Lower dioxane levels require expensive steam and/or wipe film stripping procedures.

Processing Features. Process control of reactant mol ratio is critical for optimal derived product quality because under-sulfonation usually produces unacceptable product, whereas over-sulfonation leads to undesirable side-reaction products and increased color. Comparison of product quality derived from the various equipment suppliers' units may be obscured by varying production design rates, production guarantee rates, quality of feedstocks utilized, actual operation of the plant, and by different analytical methods used in monitoring production, particularly for so-called product free oil. The azeotropic distillation method recovers only volatile components in the free oil by extraction methods which are not always quantitative, especially for ethoxylated feedstocks. The ion-exchange method is most reliable.

SO_3 Diluent Gas. In the continuous SO_3 sulfonation of LAB or BAB using 5% SO_3 in 95% dry diluent gas, the volume ratio of liquid feedstock to reaction gas is ~ 1:1.158, confirming the true nature of film reaction involved in the process. Continuous SO_3 processes based on dilute SO_3 gas systems utilize large volumes of air that must be compressed and dried preferably to a −60 to −70°C dew point. Such equipment and its operation are costly. Efforts have been made to recycle the reactor gas effluent which contains small quantities of SO_2, SO_3–H_2SO_4 mist, and organics (16,97,203,208,212). Various demister and air-filtration systems have been commercially evaluated, but to date (~2005) none have been totally successful in producing high quantity, light-colored detergent products using recycled air (203). Studies have shown that as little as 0.002% (0.5–1.0 μm) of charged feedstock or sulfonated organics carried in the exiting and filtered reactor gas stream is sufficient to contribute product discoloration problems on gas recycling. In addition, SO_2 buildup soon becomes significant (203). Air recycling does not appear viable for conventional sulfur burning sulfonation systems.

Continuous Falling Film Sulfonation Process Flow. Process flow diagrams, particularly for processes based on vaporizing liquid SO_3, reactor design details, and a critique of process operating details, are available (16,203). Figure 4 provides a process flow diagram for a typical falling film continuous SO_3 sulfonation plant with *in situ* sulfur burner SO_3 generating equipment. Air is, A, compressed; B, cooled; and C, dried to a dew point of -60 to -70°C, then supplied to the sulfur burner together with molten sulfur. SO_2 generated by the sulfur burner, D, is partially cooled (to 420°C), E, and sent to the V_2O_5 fixed-bed catalytic three-stage converter, F, generating $\sim$ 6–7% SO_3 gas stream with a typical 98.5–99% conversion. Most plants are equipped with an SO_3 adsorber system, G, capable of adsorbing SO_3 from the complete SO_3–air gas stream and that is used on plant startups or during power failure periods. This generates H_2SO_4 during said times and the stripped air then passes through a packed (dilute NaOH) scrubbing tower, H, and is vented.

After the SO_3 converter has stabilized, the 6–7% SO_3 gas stream can be further diluted with dry air, I, to provide the SO_3 reaction gas at a prescribed concentration, $\sim$ 4 vol % for LAB sulfonation and $\sim$ 2.5% for alcohol ethoxylate sulfation. The molten sulfur is accurately measured and controlled by mass flow meters. The organic feedstock is also accurately controlled by mass flow meters and a variable speed-driven gear pump. The high velocity SO_3 reaction gas and organic feedstock are introduced into the top of the sulfonation reactor, J, in cocurrent downward flow where the reaction product and gas are separated in a cyclone separator, K, then pumped to a cooler, L, and circulated back into a quench cooling reservoir at the base of the reactor, unique to Chemithon concentric reactor systems. The gas stream from the cyclone separator, M, is sent to an electrostatic precipitator (ESP), N, which removes entrained acidic organics, and then sent to the packed tower, H, where SO_2 and any SO_3 traces are adsorbed in a dilute NaOH solution and finally vented, O. Even a 99% conversion of SO_2 to SO_3 contributes $\sim$ 500 ppm SO_2 to the effluent gas.

In some competitive sulfonation systems, a more efficient liquid–gas separator system is employed, thereby eliminating the need for the ESP unit, and utilizing a demister unit along with the dilute caustic scrubber. The ESP system must be bypassed for safety reasons when used with feedstocks having relatively low boiling volatiles. Cooled sulfonic acid is continuously removed from the quench cooling loop, generally at $\sim$ 45–50°C, and pumped through digestors, P, which provide for a 10–30-min (adjustable) digestion period to help complete the reaction, after which $\sim$ 1% water is injected through an in-line mixing system, Q, to destroy residual pyro-acids and sulfonic acid anhydrides and to help stabilize acid color (16). The water injection system is bypassed when alcohol sulfation is being conducted.

Optimization of alkylbenzene sulfonic acid quality requires a subtle balancing between controlling mol ratio and maximizing digestion in order to achieve highest conversion, lowest free oil and H_2SO_4, with lightest derived product color (16,212). The resultant acid is then sent to the loop neutralization system, R, comprising a positive displacement pump, in-line alkaline mixing system, and cooling heat-exchanger loop.

Sulfonation Plant Operations and Gas Effluent. Standards governing U.S. sulfonation plant gas effluents differ depending on whether or not the plant is equipped with a H_2SO_4 scrubbing system for adsorption of SO_3 gas (see Fig. 4). The installation of the SO_3 adsorber system qualifies the plant as a sulfuric production plant which has stringent regulations. Limitations and typical effluent from the sulfonation system are as follows:

Material	Requirements	Typical
SO_2	≤ 5 ppm	<1 ppm
SO_3–H_2SO_4	≤ 10 mg/m^3	<8 mg/m^3
organic mist	≤ 20 mg/m^3	<5 mg/m^3
opacity	≤ 20 %	<5%

Most sulfonation plants monitor and control operations by computer. Sulfur-burning catalytic SO_3-generating equipment may require a 1–2-h stabilization period on startup. The unit can be kept in a standby position by maintaining heat to the unit when it is off-line. Liquid SO_3-based sulfonation plants do not require such a stabilization period, and hence are more flexible to operate than sulfur-burning sulfonation plants.

8.9. Other Continuous SO_3 Processes. The Ballestra multistirred tank continuous SO_3 cascade Sulphorex sulfonation system generally employs four stirred reactors so as to cascade from one to the next. SO_3 dry air mixture is specially proportioned to enter into each reactor, eg, 50, 25, 20, and 5%, respectively, through a sparger system. Total product residence time is estimated at 90 min on average, hence this system is primarily recommended for sulfonation of detergent alkylates and fatty methyl esters (16).

Chemithon Corporation's continuous SO_3 jet-impact sulfonation process is a commercially available unit and appears to be a combination of the diluted gaseous SO_3–organic mist and SO_3–falling film sulfonation systems. Organic feedstock and a 4–10% SO_3 dry air stream are rapidly mixed in a venturi nozzle and impinged onto a downwardly flowing stream of recycling reaction mixture operating in a cooling loop (221). The quality of derived products is reported to be only moderately less than those from falling film sulfonation processes. The unit has been utilized for various products including production of oil-soluble sulfonates.

The SO_3-based sulfonation processes, particularly continuous falling film sulfonation processes, comprise $<$ 85% of total U.S. sulfonation plant capacity. This is expected to increase, particularly based on sulfur burner SO_3 generation sulfonation systems. Falling film continuous SO_3 sulfonation processes dominate because of greater versatility in processing a variety of feedstocks, lower reagent costs, elimination of by-product streams, and capability for direct production of high purity, high quality products (16,203). Details of a small laboratory apparatus for the experimental falling film continuous SO_3 sulfonation have been published (222).

8.10. Recent Developments in SO_3 Film Sulfonation Technology. During the past decade or so, a significant number of pertinent technical publications and patents were focused primarily on equipment and process fine points connected with SO_3 film sulfonation, including LAB conversion to LAS (and resulting derived product quality, by-product formation, feedstock quality, reaction mechanisms), as well as AOS and MES process developments (208–211,213,220,223–247).

Reactor design and operation features have been reviewed (210,211,224, 231,248). Several process improvement patents have been issued recently (215,216,240,243). The use of a corrogated surface reactor has been described (238) and patented (241,242). Substantial improvements in LAB feedstocks have been made and reviewed recently (227,230,231). Sulfonate color has been correlated with quality parameters, eg, bromine index, heavy alkylate content, iron, alkylate storage temperature, and alkylate exposure to light (227). Current alkylate sources have bromine indexs of 2–5. Obviously, it is essential to limit or prevent moisture pick-up in organic feedstocks, since water reaction with SO_3 will not only result in elevated H_2SO_4 content in product, but will also impact the effective SO_3/organic mole ratio.

Several studies have been published on optimization of process variables for the sulfonation of LAB (220,226,228,229). The objectives of the process optimization depends on whether the goal is to maximize the degree of conversion with its economic advantage, or perhaps best quality considerations such as product color, or a combination of both goals. Process optimzation includes process parameters both for sulfonation and the subsequent digestion step. One recent study that used the conventional digestion of $\sim$ 20 min at 45–50°C (16) varied mole ratio of SO_3:LAB from 1.0:1.0 to 1.09:1.0, and compared a commercial Chemithon system to a Ballestra multitube reactor system. Maximum conversions of 98.4% were obtained with 1.6% free oil for both systems at 1.04:1.0 mole ratio, with some drop-off in conversion at higher SO_3 input (228). Another recent pilot plant conversion study also showed a maximum conversion of 98.1% with 1.2% free oil at an SO_3/LAB mole ratio of 1.04–1.05:1.0, also with a slight drop-off in actives with higher SO_3 input. That study used a 1-h digestion at 40°C. The greater the excess of SO_3 used, the greater the resulting H_2SO_4 content of the acid and the greater the product color. This study also showed the effect of varying digestion time and temperature on derived product color (226). The apparent drop-off in actives with increased SO_3 input in these two optimzation studies is perhaps explained by the potential formation of some disulfonate, which has been cited in the literature (16,210). The LAS disulfonates would not be determined by the standard Epton titration. Another proposed explanation for reduced actives with increased SO_3 input is increased sulfone formation (219).

A 1999 German patent claims an improved process for SO_3 film sulfonation of LAB using a 5–15-h digestion at 40–45°C before stabilization, yielding a 97.8% conversion (237). In another 2003 pilot plant optimization study, sulfonation at an SO_3/LAB mole ratio of 1.02:1.0 was followed by a prolonged digestion at 40°C. This extended digestion increased the LAS acid actives from 95.2% at 40 min (5% Klett color of 3) to 97.5% at 10 h (5% Klett color of 20). The H_2SO_4 content was found to decrease from 2.1 to 0.8% over the course of the digestion (220,229). This study postulated that there were four possible sequencing steps during the digestion based on reaction kinetic measurements, mostly involving H_2SO_4. The study concluded that conventional aging was insufficient to give maximum conversion and recommended for commercial production that a 4-h digstion be utilized at $\sim$ 45°C, followed by stabilization with only 0.3 wt.% water.

Analytical methods using high performance liquid chromatography (HPLC) have confirmed the presence of sulfonic acid anhydrides, sulfones and unsulfonated alkylate in the free oils of freshly produced LAS acid from commercial film sulfonators (223). A subsequent study by the same authors described the effect of mole ratio of SO_3:LAB on the composition of free oil in a pilot plant SO_3 film reactor (224), using HPLC, etc. This study concluded that as the ratio of SO_3 to LAB was increased from 1.0 to 1.1, there was an increase in anhydrides and a decreased in non-sulfonated LAB in freshly produced and analyzed acid, while sulfone content was independent of SO_3 input. Sulfone formation appears to be promoted by high temperature (16). Typical sulfone content of LAS acid appears to be $\sim$ 0.8 wt.%. This same group conducted further studies on LAS acid digestion and subsequent stabilization (or hydrolysis) with water (219). These investigators took freshly produced LAS acid from a commercial SO_3 film reactor and subjected the acid to an abnormal digestion/aging step at 60°C for multiple hours (0.5–2.5 h), followed by 1% water addition also at 60°C. Conventionally, water addition completes hydrolysis of any residual sulfonic acid anhydrides and quenches any remaining pyroacids. The HPLC analysis established the disappearance of anhydride, but also demonstrated that there was a surprising $\sim$ 25% reduction of sulfones in the free oil, suggesting that sulfone hydrolyzed to produce more active. This hydrolysis reaction has been proposed previously (220). As noted, these processing conditions were abnormal, and the effect on conversion is minimal in any event.

If the sulfone component in the sulfonic acid is essentially intransigent, this would typically equate to $\sim$ 0.6% as alkylate, and since most commercial alkylate contains perhaps $\sim$ 0.3% unsulfonatable paraffins, this means that maximum or ultimate conversion would be limited to $\sim$ 99.2%. Obviously, the ultimate conversion of LAB to LAS acid could be further increased if sulfone levels could be suppressed. The foregoing studies on process and product optimization, together with the improved quality of LAB (for improved product color), provides some flexibility in commercial processing. Never-the-less, it should be noted that over-sulfonation is undesirable (because of high byproducts and color problems), and that limiting the SO_3/LAB mole ratio to $\sim$ 1.02–1.03, combined with a suitable digestion step, represents a good compromise. Digestion for a longer time and/or at higher temperatures has an adverse effect on product color.

General overviews of sulfonation and sulfation processes were published recently (220,232,244), as well as one on sulfur burning SO_3 generating technology (214). A sulfonation process control system critique was recently published (236). Several reports on recent developments on AOS production have been issued (233,246). Several papers have also appeared recently in the technical literature pertaining to the manufacture of MES products (234,235,247).

Two recent reports characterized the organic film in continuous SO_3-film reactors as “prodominantly laminar” (220,229). In addition, the modeling of falling film sulfonation in terms of laminar flow has been published (220,248). Two opposing semantic polemic responses were then published (213,245). Substantial evidence was presented in support of the position that the film in falling film sulfonation–sulfation is highly turbulent (203,245,249), which was also the conclusion reached by a U.S. Federal District Court judge in a patent infringment lawsuit (203,250). One of the most compelling pieces of evidence was a simulated process demonstration photograph showing that the organic film in the presence of high velocity gas produced “repetitive waves that were over four-times higher than the average film-thickness”, with corresponding alternating very thin troughs (250,251), thereby indicating a highly turbulent film.

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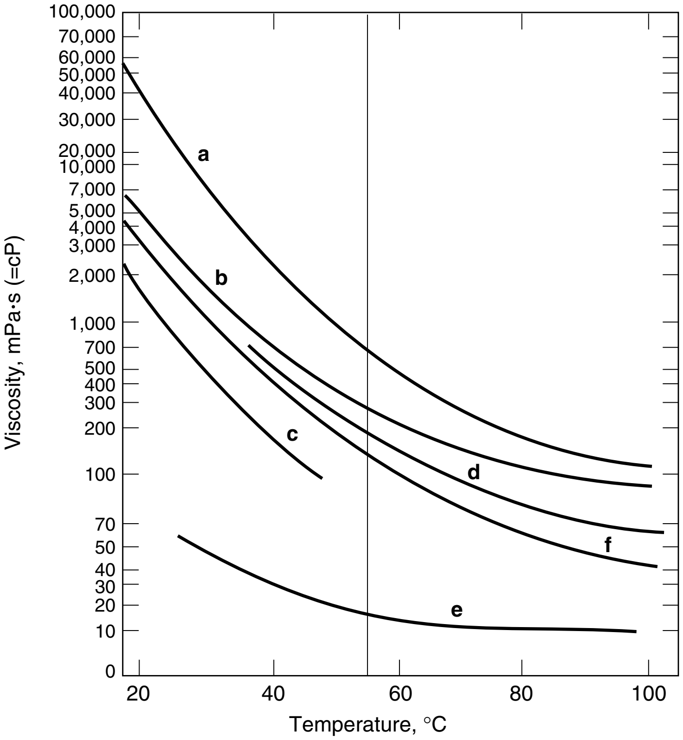


Fig. 1. Sulfonated and sulfated acid products viscosities after 98% conversions at varying temperatures where the vertical line indicates the maximum temperature for batch sulfonation using SO_3 to minimize color deterioration; lines **a**–**c** represent branched C_{12} alkyl benzene (BAB):sulfonic acid from SO_3, oleum (settled), and oleum (whole mixture), respectively; lines **d** and **e**, lauryl alcohol 3-ethoxylate sulfuric ester (SO_3) and lauryl alcohol sulfuric ester (SO_3), respectively; and line **f**, linear C_{12} alkyl benzene (LAB) sulfonic acid (SO_3).

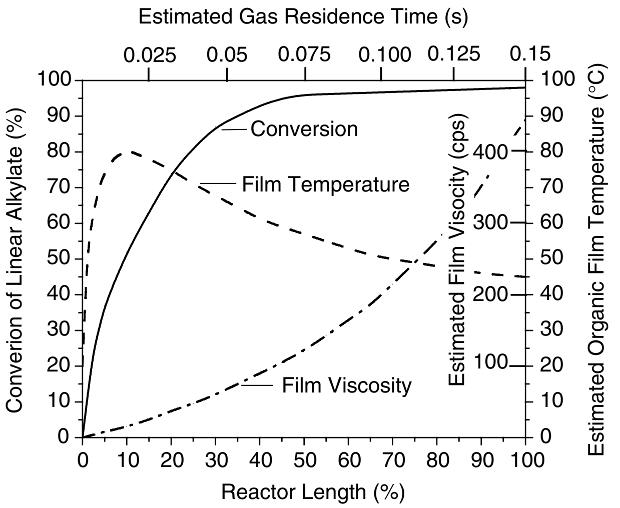


Fig. 2. Relationship of linear alkylate to sulfonic acid conversion, estimated film temperature, and estimated film viscosity to reactor length and to estimated gas residence time for Ballestra Continous SO_3 falling film reactor system. Conversion and film temperature profiles courtesy of Ballestra SpA. Film viscosity data courtesy of Springer Science and Business Media.

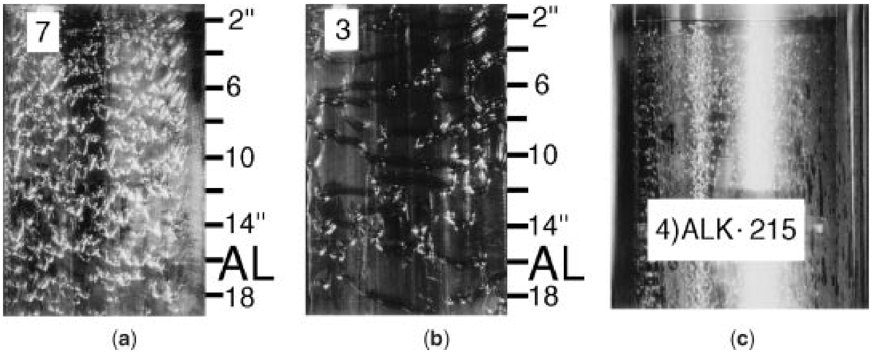


Fig. 3. High speed photos of organic film–high velocity air dynamics in falling film sulfonation process: (**a**) and (**b**) are vertical flat plate organic–air dynamics where (**a**) shows BAB–air at top; (**b**) BAB sulfonic acid–air at bottom of reactor; (**c**) simulated Allied-type concentric reactor inner-cylindrical reaction surface showing BAB–high velocity air (see Table 9) (1 in. = 2.54 cm).

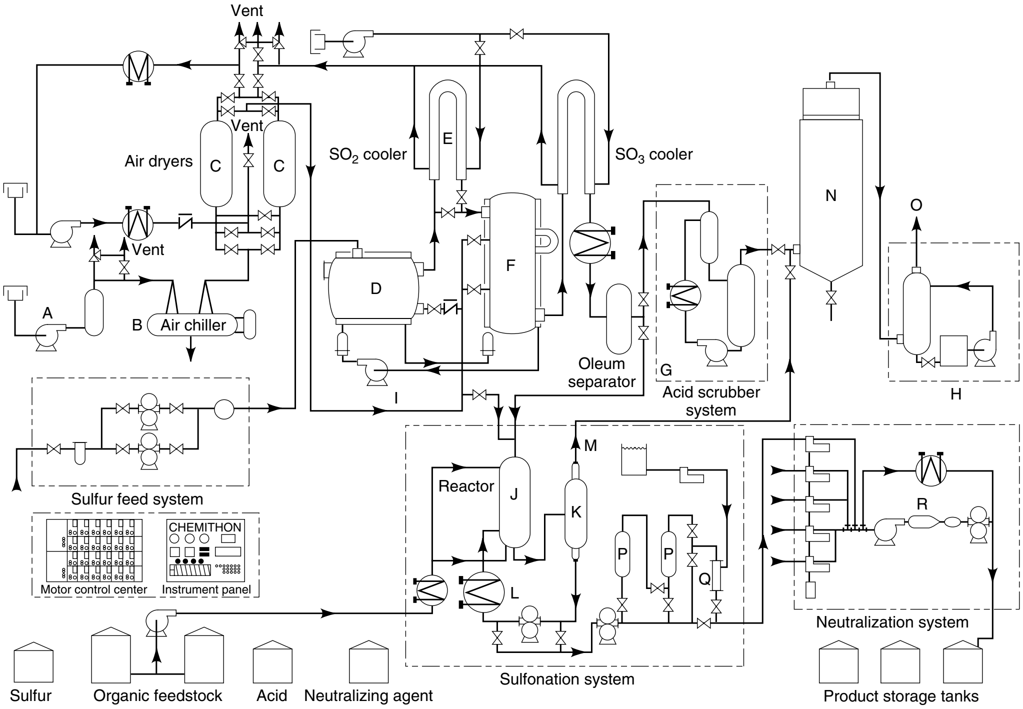


Fig. 4. Process flow diagram for a continuous falling film SO_3 sulfonation plant, equipped with a sulfur-burning SO_3 converter unit. (See text.) (Courtesy of Chemithon Corp.)

Table 1. **U.S. Consumption and Pricing for Several Classes of Sulfonated and Sulfated Products**

	Volume		Pricing[a]		
Product class	metric tons	year	$/lb	year	References
linear alkylbenzene sulfonates (LAS)	317,500	2003	0.85	2004	12
alcohol ether sulfates and alcohol sulfates	616,000	2003	2.07–2.14	2004	12
α-olefin sulfonates (AOS)	16,500	2003	1.38	2004	12
methyl ester sulfonates (MES)	16,300	2003	1.33	2004	7,12
lignosulfonates	290,300	2001	0.068–0.168	2002	11
alkyl naphthalene sulfonates	34,900	2003	1.01	2004	12,13
sulfonate-based corrosion inhibitors[b]	12,200	2002	1.34	2002	10
hydrotropes (simple aromatic sulfonates)	35,900	2003	0.89	2004	10
sweeteners	1000	2002	2.00–26.00	2003	14

[a] List price: actual prices in commerce typically significantly lower.

[b] Petroleum sulfonates, synthetic sulfonates, and dialkylnaphthalene sulfonates used in oil field production and metalworking.

Table 2. **Reagents for Direct Sulfonation and Sulfation Reactions**[a,b]

Reagent	Formula	Physical form	Cost $/lb	U.S. mfg[c]	U.S. plants[c]	Advantages	Disadvantages	Applications
sulfur trioxide	SO_3	liquid	0.12	1	2	low cost, concentrated reagent	extremely reactive; charring	supply for dilute gas SO_3 streams
sulfur burning	SO_3	gas *in situ*, 3–8% SO_3	0.03[d]	84	177	lowest cost SO_3 produced *in situ*; preferred reagent	catalyst requires startup time; higher investment cost	nearly every sulfonation and sulfation reaction
chlorosulfonic acid	$ClSO_3H$	liquid	0.20	2	2	stoichiometric reactions	expensive; produces HCl gas	alcohol sulfation, dyes, etc.
oleum	$H_2SO_4 \cdot xSO_3$	liquid: 20% SO_3 60% SO_3	0.07 0.10	5	11	low cost	reactions not stoichiometric; 3–4 mol generally required	dyes, alkylated aromatic sulfonation; continuous sulfation of alcohols
sulfuric acid	H_2SO_4	liquid	0.05	50	73	low cost, easily handable	reaction not stoichiometric; 3–4 mol generally required	hydrotrope sulfonation of aromatics using azeotropic water removal, etc.
sodium bisulfite	$NaHSO_3$	solid 38% liquid	0.32 0.30	2	2	simple processing	higher cost, except for sulfur burning	sulfosuccinates, lignin, olefins, Streker reaction
sodium sulfite	Na_2SO_3	soild	0.27	5	5	simple processing	higher cost	Streker reaction, etc.
sulfamic acid	H_2NSO_3H	solid	0.43	1	1	stoichiometric reaction, mild, simple	high cost; limited to NH_4 salt	small specialties, sulfations
sulfur dioxide and chlorine	SO_2, Cl_2	gases	0.72 0.16	6 16	7 38	few, relatively inexpensive	not generally stoichiometric; need catalyst	chlorosulfonation of paraffins
sulfur dioxide and oxygen	SO_2, O_2	gases	0.72 0.12 c.ft	6	7	few, inexpensive	not stoichiometric; need catalyst	sulfoxidation of paraffins

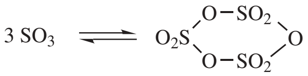
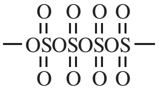
[a] In order of descending reactivity.

[b] Unless noted, prices based on November 21, 2005 Chemical Market Reporter data or manufacturer list price.

[c] Directory of Chemical Producers: United States, Access Intelligence, 2005; Directory of World Chemical Producers, Chemical Information Services, http://www.chemcialinfo.com

[d] September 26, 2005 Chemical Market Reporter data.

Table 3. **Polymers of Sulfur Trioxide**

Parameter	γ	β	α
probable structure[a]			Similar to β-form, chains joined in layered structure
physical form	liquid or vitreous	silky fibers	fibrous needles
Equilibrium melting point, °C	16.8[b]	32.5	62.3
vapor pressure, kPa[c]			
At −3.9°C	28.3	24.1	3.4
23.9°C	190.3	166.2	62.0
51.7°C	908.0	908.0	699.1
79.4°C	3280.6	3280.6	3280.6

[a] As suggested by electron diffraction patterns, ir, and Raman spectra.

[b] bp = 44.7°C.

[c] To convert kPa to psi, multiply by 0.145.

Table 4. **Composition of Sulfuric Acid, Oleum, and Liquid SO_3 Sulfonating Reagents**

No.	Designation	Free SO_3, %	Total SO_3, %	H_2SO_4, %	Equivalence to 100% H_2SO_4, %	Sp gr
1	66° Baumé[a]		76.08	93.2	93.2	1.8354
2	H_2SO_4, conc		78.37	96.0	96.0	1.8427
3	H_2SO_4, conc		80.0	98.0	98.0	1.8437
4	100% H_2SO_4		81.63	100.0	100.0	1.8391
5	100.6% H_2SO_4	3	82.18	97.0	100.6	1.855
6	Oleum, 20%	20	85.30	80.0	104.5	1.915
7	Oleum 70%[b]	70	94.49	30.0	115.75	1.982
8	liquid SO_3[c]	99.7	99.80		122.5	1.9224

[a] Baumé concentration is based on the hydrometric method; °Bé = 145−145/sp gr.

[b] 70% Oleum is used to provide gaseous SO_3 via stripping.

[c] Stabilized liquid SO_3 contains 0.2% stabilizer.

Table 5. **Comparison of Sulfuric Acid and Gaseous SO_3 Sulfonation Reagents for Sulfonating Aromatic Hydrocarbons**[a]

Comparative factors	Sulfuric acid–oleum	SO_3 (g)
aromatic sulfonation	water by-product produced	addition Rx; no water produced
mole ratio, Rx completion	~3–4 mol; excess reagent not critical	~1 mol; excess reagent quite critical
reagent miscibility	immiscible with organics; 2 immiscible liquids Rx	liquid-gas two-phase Rx
solubility, organic solvents	immiscible	miscible
mechanical agitation	essential	not needed using high velocity gaseous falling film reaction
reaction temperature	varied (0–50°C); basis of product color quality; solvents often used to reduce viscosity	falling film process (short contact times) allows higher reaction temperature profile, avoiding need for solvents
reaction mixture viscosity	relatively low	higher
reaction rate	slow	instantaneous
heat of sulfonation, alkylbenzene kJ/mol[b]	−112	−170
heat input	heat for completion	strongly exothermic, no heat required
heat exchange	low temperature Rx dictates refrigerated brine cooling system	film sulfonation uses ambient H_2O cooling; highly efficient
side reactions	minor	often extensive
derived product color	lighter	darker, except falling film system
final derived sulfonic acid	Rx mixture separates, H_2O often added to facilitate; color bodies partially removed into separated spent H_2SO_4	Rx mixture homogenous
generation of spend acid/1.0 kg sulfonic acid for disposal, kg	0.75–1.14	0
reagent boiling point, °C	290–317	44.5

[a] Rx = reaction.

[b] To convert J to cal, divide by 4.184.

Table 6. **Indirect Sulfonating Reagents**

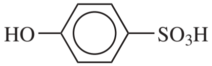
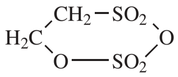
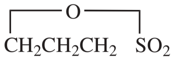
Reagent name	CAS Number	Chemical structure	Reaction	Reference for example
sodium 2-hydroxy-ethanesulfonate	[1562-00-1]	$HOCH_2CH_2SO_3Na$	esterification	22
sodium *N*-methyltaurinate	[4316-74-9]	 $CH_3\overset{H}{N}CH_2CH_2SO_3Na$	amidification	22
sodium chloromethanesulfonate	[10352-63-3]	$ClCH_2SO_3Na$	condensation	23
sulfoacetic acid	[123-43-3]	HSO_3CH_2COOH	esterification	24
4-hydroxybenzene-sulfonic acid	[98-67-9]		esterification	25
carbyl sulfate	[503-41-3]		condensation	26
sodium hydroxymethane-sulfonate	[870-72-4]	$HOCH_2SO_3Na$	sulfoalkylation	27
1,3-propane sultone	[1120-71-4]		sulfoalkylation	28
sodium vinylsulfonate	[3039-83-6]	$CH_2{=}CHSO_3Na$	polymerization, sulfoalkylation	29

Table 6. (*Continued*)

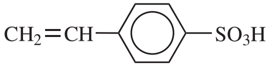
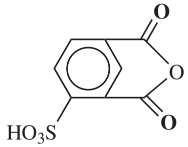
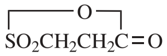
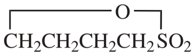
Reagent name	CAS Number	Chemical structure	Reaction	Reference for example
4-ethenylbenzenesulfonic acid	[98-70-4]		polymerization	30
4-sulfophthalic anhydride	[134-08-7]		condensation, esterification, etc	31
sodium 2-cyanoethane-sulfonate	[513-15-5]	$N\equiv CCH_2SO_3Na$	hydrolysis	32
3-sulfopropionic anhydride	[5961-88-6]	 $SO_2CH_2CH_2C{=}O$ (ring through O)	sulfoalkylation	33
1,4-butane sultone	[1633-83-6]	 $CH_2CH_2CH_2CH_2SO_2$	sulfoalkylation	28

Table 7. **Heats of Sulfonation and Sulfation Reactions Using Gaseous SO_3 and Oleum Reagents**[a]

Organic feedstock	Reagent	Reaction	$\Delta H = \text{kJ/mol}$[b]
alkylbenzenes	gaseous SO_3	sulfonation	−170
primary fatty alcohols	gaseous SO_3	sulfation	−150
ethoxylated alcohols	gaseous SO_3	sulfation	−150
α-olefins	gaseous SO_3	sulfonation	−210
alkylbenzenes	oleum	sulfonation	−112

[a] Ref. 16.

[b] To convert J to cal, divide by 4.184.

Table 8. **Comparative Summary of Various Batch and Continuous Detergent Alkylate Sulfonation Processes Using Oleum and Gaseous SO_3**

Line	Sulfonation process examples	A	B	C
1	source	Kircher[a]	Chemithon	Stepan
2	sulfonation mode	batch	continuous	continuous
3	sulfonation reagent	20% oleum	20% oleum	SO_3 gas
4	alkylate type	BAB[b]	LAB[c]	LAB[c]
5	reagent/alkylate wt ratio	1.25:1.0	1.18:1.0	0.344:1.0
6	reagent/alkylate mol ratio	3.16:1.0	3.0:1.0	1.02:1.0
7	sulfonation temp, °C	25	54	54[d]
8	digestion temp, °C	25	54	54
9	acid composition after digestion, wt%			
10	active acid	58.3	61.3	97.5[e]
11	H_2SO_4	40.0	37.0	1.3[e]
12	free oil	0.9	0.7	1.2[e]
13	water	0.8	1.0	0.0
14	neutralized product: Na sulfonate:Na_2SO_4, wt%	51.8:48.2	62.3:37.7	98.2:1.8
15	neutralized product if water addition to acid phase separation step is used: Na sulfonate:Na_2SO_4, wt%	90.2:9.8	87.8:12.2	98.2:1.8
16	"spent acid" generated: parts/1 part of separated sulfonic acid	0.75	0.79	0.0
17	Na sulfonate color: 5% Klett	40	30	15

[a] Ref. 197.

[b] BAB = branched alkylbenzene.

[c] LAB = linear alkylbenzene.

[d] Film reactor outlet temperature.

[e] wt.% on a "dry" basis: calculated after addition of 1.0% water for stabilization.

Table 9. **Estimated Typical Operating Conditions and Rates of Commercial Continuous SO_3 Falling Film Sulfonation Processes for Sulfonation of LAB and Lauryl Alcohol-3 mol Ethoxylate Feedstocks**[a]

Falling film SO_3 suppliers	Meccaniche moderne (Allied Design)	Chemithon Corp.	Ballestra SpA	Meccaniche Moderne	Impianti per Industrie dei Tensioattivi
commercial designation	monotube	annular film reactor	Sulphorex F	multitube	multitube
Reactor type	concentric	concentric	multitube	multitube	multitube
LAB-sulfonic acid, kg/h	2,540	5,214[b]	6,040	4,680	5,000
annual production rate LAB-sulfonic acid 8000 h, metric tons[c]	20,000	41,712	48,318	37,250	40,000
reaction tubes	2	2	142	150	120
tube(s) diameter, cm	102.8, 99.3	121.9, 120.5	2.54	2.67	2.80
concentric reactor:					
wall spacing, cm	3.50	1.44			
gap (1/2 spacing), cm	1.65	0.72			
tube length, m	6.0	2.0	6.0	6.0	6.0
reactor tubes, circumference, m	6.35	7.62	7.98	11.0	10.6
organic loading, kg/(h·mm)	0.4	0.4	0.4	0.32	0.35
calculated SO_3 conc, vol/vol, %	3.3	4.0	4.0	4.2	4.5
nominal reaction gas velocity,[d] m/s	34.1	74.9	39.1	34.1	20.2
gas velocity , km/h (mph)	124.6 (77.5)	269 (167)	140.0 (87.5)	130.1 (81.3)	88.5 (55.0)
estimated gaseous residence time, s	0.17	0.09	0.15	0.16	0.24
cooling jacket zones	3	2	3	3	1
cooling system:					
surface, m^2	38.1	15.2	67.9	21.2	63.3

Table 9. (*Continued*)

Falling film SO_3 suppliers	Meccaniche moderne (Allied Design)	Chemithon Corp.	Ballestra SpA	Meccaniche Moderne	Impianti per Industrie dei Tensioattivi
surface per kg/min LAB sulfonic acid, m^2	0.67	0.225	0.675	0.96	0.76
postreactor quench	no	yes	no	no	no
recommended alcohol-3M-ethoxylate loading kg/(h·mm)	0.3	0.28	0.34	0.28	0.27
calculated corresponding SO_3 conc, vol/vol, %	1.9	2.6	2.5	2.7	2.5

[a] Estimates based on published and industry information sources for production of linear alkyl (C12) benzene sulfonic acid and lauryl-3 mol ethoxy sulfate.

[b] Chemithon can supply two units in parallel using single gas supply and single downstream system, hence doubling the capacity.

[c] Suppliers process equipment and rates; higher capacity units may be available.

[d] Nominal reaction gas velocity calculated in the absence of organics.

[e] Typical gaseous residence time calculated in absence of organics.

[f] Multiple zones for outer reactor wall, one for inner wall.

[g] At constant air supply.