SULFONATION

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THE present review covers contributions to the art of sulfonation reported in the published literature from about 1941 to the forepart of 1947. In general, this review embraces material reported in *Chemical Abstracts* as well as information about sulfonation processes used in Germany as described in various government reports—e.g., British Intelligence Objectives Sub-Committee Final Reports (BIOS reports), Field Information Agency Technical Final Reports of the U. S. Government (FIAT reports), and others. The review is limited to reactions which form compounds wherein the sulfonic acid group—SO_3H—is bonded directly to a carbon or nitrogen atom of an organic compound. Thus it embraces sulfochlorination methods where the sulfonyl chlorides formed thereby are transformed by hydrolysis to sulfonic acids, but does not include sulfation reactions, as these give rise to compounds wherein the —SO_3H group is bonded to an oxygen atom, viz., —O—SO_3H. The writer has made an attempt to cover all the important literature on sulfonation within the present scope. He would gratefully appreciate receiving information concerning significant material that has been omitted.

THEORETICAL CONSIDERATIONS

Aliphatic Compounds

SATURATED

Direct Sulfonation. WITH COMPOUNDS CONTAINING SULFUR TRIOXIDE. Paraffin hydrocarbons can be sulfonated only under vigorous reaction conditions which usually give rise to both sulfonation and oxidation products (*276*, *286*). For this reason, direct sulfonation methods using compounds containing sulfur trioxide have found relatively limited application except for the preparations of so-called mahogany and green sulfonic acids from petroleum, and most of the work on sulfonation of paraffin hydrocarbons has concerned the use of other sulfonating agents—e.g., sulfur dioxide and chlorine, sulfur dioxide and oxygen, etc., as discussed below. Taylor (*286*) discloses an improved method for sulfonating a saturated aliphatic hydrocarbon or chlorinated derivative thereof containing eight to twenty carbon atoms per molecule with a strong sulfonating agent, such as oleum. The sulfonation is performed in the presence of an organic carbonyl compound, such as ethyl acetate, which is said to inhibit oxidation and promote the sulfonation reaction. A recent patent (*285*) describes a process whereby a paraffin hydrocarbon containing at least three carbon atoms reacts with sulfur trioxide in the vapor phase to yield a mixture of products containing one or more sulfone, sulfate, sulfonic acid, and sulfonic anhydride groups. Petroleum distillates have been treated with sulfuric acid or oleum to form mahogany and green sulfonic acids, but these are derived chiefly from the alicyclic and aliphatic-aromatic constituents of the distillates (*6*, *12*, *37*, *38*, *39*, *125*, *126*, *201–203*, *258*, *260*, *268*, *298*, *299*). Production, classification, and uses of petroleum sulfonic acids have been reviewed (*58*, *59*, *61*, *248*).

Practically quantitative yields of sulfonic acids of fatty acids, anhydrides, and aliphatic ketones are produced by effecting the sulfonation with strong sulfonating agents in the presence of a tertiary nitrogen compound, such as pyridine, amounting to as little as 0.01% of the weight of the sulfonating agent (*67*). It has been found beneficial to sulfonate saturated aliphatic ketones containing at least six carbon atoms in an "active solvent," such as a derivative of a carboxylic acid of low molecular weight, particularly an anhydride, halide, amide, nitrite, or ether (*163*). Liquid sulfur dioxide is also said to be an advantageous solvent for carrying out the sulfonation of saturated higher fatty acids and dialkyl ketones (*68*). Methane trisulfonic acid, which is an unusual compound by virtue of the three sulfonic acid groups attached to the same carbon atom, and is an important commercial catalyst for esterification of acetylene with carboxylic acids, can now be obtained in approximately 80% yield by addition of acetic acid or anhydride to four to seven times its weight of 65% oleum at 65° to 100° C. (*62*). Goldberg (*123*) discloses a new method for preparing isethionic acid and its salts in high yield, which consists of adding 60% oleum to ethyl sulfate below 10° C. and hydrolyzing the reaction product. Campaigne and Suter (*57*) reviewed Bistrzycki's (*35*) work on the cleavage of carbon monoxide from tertiary carboxylic acids in concentrated sulfuric acid. They determined the structure of two previously unidentified sulfonation products obtained from trimethyl- and dimethylphenylacetic acids and proposed a reaction mechanism for their formation. These products are 2-methylpropene-1,3-disulfonic acid and *o*-sulfo-α-methylstyrene polymers.

Reychler (*252*) sulfonated camphor to give camphor-ω-sulfonic acid. Using Reychler's method to sulfonate natural and artificial camphor, Poggi and Polverini (*243*) obtained maximum yields of 66.25% in 104 days for natural camphor and 57.60% in 35 days for synthetic camphor. Lipp and Knapp (*206*) reported that the reaction mechanism involves 1-hydroxycamphene which sulfonates more readily than camphor itself. Among several methods for sulfonating α-bromocamphor, Guha and Bhattacharyya (*130*) discovered that chlorosulfonic acid yielded *d*-α-bromo-π-camphor sulfonate most rapidly and economically.

SULFURYL CHLORIDE, SULFUR DIOXIDE–CHLORINE (SULFOCHLORINATION). Numerous recent studies of sulfonation of paraffin hydrocarbons by means of sulfuryl chloride, or sulfur dioxide and chlorine (Reed reaction), have been reported chiefly in the patent literature, and attest to interest in these methods, particularly for producing wetting, etc., agents (*8–11*, *79*, *87*, *97*, *116*, *128*, *129*, *144*, *146–148*, *168*, *250*, *265*). Several reviews on this subject have appeared (*51*, *95*, *229*, *265*). In general, this method produces a mixture of sulfochlorinated isomers—i.e., alkyl monosulfonyl chlorides, chloroalkyl monosulfonyl chlorides, alkyl polysulfonylchlorides, and chloroalkyl polysulfonyl chlorides, together with alkyl chlorides and alkyl polychlorides (*219*); however, under carefully controlled conditions it yields alkyl monosulfonylchlorides almost exclusively (*8*, *26*, *31*, *168*). Ultraviolet light has generally been used as the catalyst, at times in conjunction with an organic base and a solvent. Grubb and Tucker (*128*, *129*) patented the method of effecting the reaction in the dark, employing as a catalyst an organic peroxide alone or in conjunction with an organic nitrogen compound, and thereby avoiding technically difficult arrangements for supplying adequate actinic illumination.

Detrick and Hamilton (*79*) found that the reaction could be effected in the presence of iron if 0.1 to 1.0% of an organic compound containing the radical of an acid of phosphorus were present. A continuous process employing liquid sulfur dioxide as a solvent has been described (*148*). Asinger (*8*) obtained a preponderance of monosubstitution products by interrupting the reaction when approximately 50% complete. By proper choice of hydrolysis conditions, he was able to effect a clean separation of unreacted oil suitable for recycling. The I.G. Farbenindustrie manufactured Mersolates—i.e., mixtures of C_{15} and C_{16} alkyl sulfonates—by the Reed process (*26, 31, 34, 97*). Fox (*117*) obtained exonuclear sulfonic acid derivatives of aralkanes by sulfochlorination—e.g., dodecylbenzene exosodium sulfonate. Detailed studies have been reported for the reaction of sulfur dioxide and chlorine on propane (*11*), butane (*16*), isobutane (*9*), and heptane (*265*). Helberger (*144*) has reported on the reaction mechanism. Schumacher and Stauff (*265*) reported in more detail studies of the reaction mechanism of the photochemical formation of sulfonyl chlorides by sulfuryl chloride in the presence of pyridine, and the photochemical sulfochlorination with mixtures of sulfur dioxide and chlorine. They suggest a free radical mechanism.

The foregoing sulfochlorination reaction has also been applied to derivatives of paraffin hydrocarbons. Alkyl halides undergo reaction with sulfur dioxide and chlorine to form sulfonyl chloride derivatives (*151*). Aliphatic alcohols with more than six carbon atoms yield true sulfonates on reaction with sulfur dioxide and chlorine, whereas with strong sulfonating agents they yield sulfates (*257*). Kharasch (*189*) patented the reaction of sulfuryl chloride with aliphatic carboxylic acids containing three to six carbon atoms; under anhydrous conditions the β-sulfocarboxylic acid anhydride results, whereas the free acid is formed in yields up to 77% when a small amount of water is present.

SULFUR DIOXIDE AND OXYGEN. The foreign patent literature (*158–161, 169*) discloses a new method for introducing the sulfonic acid group into aliphatic saturated compounds by use of sulfur dioxide and oxygen in the presence of catalysts, such as photoactive rays (*158, 169*), organic per acids (*159*), and ozone (*160*). This method was discovered and exploited commercially by the I. G. Farbenindustrie, Hoechst, and is discussed more fully below under Technical Developments (*26, 31*).

Substitution or Addition Reactions with Sulfites and Bisulfites. The replacement of a halogen atom by a sulfonic acid or a sulfonate group by reaction with a salt of sulfurous acid (Strecker reaction) is still applied extensively, particularly in industry. A wide variety of aliphatic and substituted aliphatic sulfonates, many possessing detergent, wetting, and emulsifying properties, have been prepared by this method (*55, 56, 62, 80, 84, 86, 88, 90, 108, 138, 139, 164, 185, 226, 235, 249, 263, 288, 297, 312*). The usual procedure is to heat a halogen compound in a polar solvent with a salt of sulfurous acid at atmospheric or superatmospheric pressure until reaction is complete. Nitrosyl chloride olefin adducts, a class of compounds which lately has attracted interest, yield derivatives containing both sulfonate and sulfamate groups (*17–21*). Conversion of epichlorohydrin with sodium sulfite to sodium propylene oxide sulfonate in 71% yield has been patented (*264*).

Formation of aliphatic sulfonic acids by reaction of sulfites and bisulfites with nonhalogenated compounds has also been reported. The reaction of alkylene sulfides with alkali bisulfites produces aliphatic mercaptosulfonates in 85% yield (*293*). McIlwain (*210*) declares that aliphatic aldehydes react with aqueous alkali sulfites and ammonium hydroxide, or ammonium sulfite, to yield α-aminosulfonic acids.

Sulfonate products free from objectionable odor and substantially free from nonsulfonated or unsaponified material are obtained by heating a mixture of an aliphatic alcohol, ester, or ester salt, and an alkali sulfite in the presence of a flux, such as fatty acid soap, while agitating the mixture, especially by passing a current of an inert gas through it (*255*).

Several investigations are concerned with the sulfonation of cellulose and hemicellulose degradation products—i.e., sugars, cellobiose, etc.—by sulfite treatment (*1, 135, 136, 143*). Pure sulfonic acid derivatives of holocellulose and simple sugars, such as glucose, galactose, and fructose, can be prepared by pressure heating with sulfite-cooking acid (bisulfite and free sulfur dioxide) but products containing sulfur could not be obtained from lactose and cellobiose (*143*). Formation and constitution of sugar sulfonic acids have been reviewed (*1*).

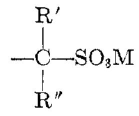
Oxidation of Sulfur Compounds. Sulfonic acids can be obtained by oxidation of organic compounds containing sulfur of lower valence. The method, though not new, is of interest because the corresponding sulfonic acids are usually obtained in good quality and free from isomers. Ordinarily, nitric acid is employed to effect oxidation, but other agents, such as hydrogen peroxide and potassium permanganate, have been used. The oxidation of dialkyl disulfides and aliphatic mono- and dithiols to sulfonic acids has been described in the patent literature (*4, 78, 86, 96, 249*). The treatment of sulfurized hydrocarbons of the formula $C_NH_{2N}S_3$ containing more than four carbon atoms with 70% nitric acid at 60° to 80° C. is said to produce high yields of the corresponding hydroxyl-substituted monosulfonic acids (*305*). Aliphatic disulfides, such as dodecyl disulfide, have been converted to sulfonyl chlorides by chlorination in aqueous medium (*155*). The chlorination of benzothiosulfates in aqueous solution in the presence of a lower fatty acid to give high yields of substantially pure benzyl sulfonyl chlorides has been patented (*82*).

Johnson and Sprague (*182*) introduced a useful method for obtaining aliphatic sulfonyl halides by halogenating *S*-alkyl thioureas (readily obtainable from alkyl halides and thiourea, or alcohols and salts of thiourea) in aqueous solution. Suter (*277*) reported that this method produces good yields from primary [sic] alkyl isothioureas, low yields from secondary alkyl isothioureas, and zero yields from *tert*-butyl isothiourea and other miscellaneous isothiourea derivatives according to the following reaction:

$$\mathrm{RSC\,(NH_2) = NH + 3Cl_2 + 2H_2O \longrightarrow RSO_2Cl + 4HCl + Cl\,C(NH_2)NH}$$

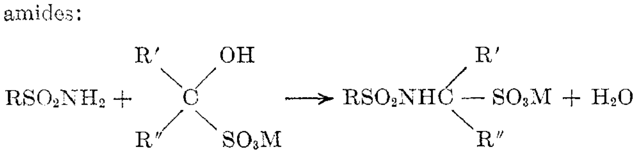
Nelles (*228*) also reviewed previous work in this field. This method has been applied recently to prepare polyalkylene ether disulfonyl halides—e.g., 2,2′-disulfonyl chloride diethyl ether—which was obtained in 90% yield (*181*). The preparation of ω-monosulfonated aliphatic carboxylic acids by this route has been patented (*84*).

Aldehyde and Ketone Bisulfites. Addition products of aldehydes and ketones with acid salts of sulfurous acid have been used



$$-\overset{\displaystyle R'}{\underset{\displaystyle R''}{C}}-SO_3M$$

to introduce the group into amines, sulfonamides, and carboxamides:

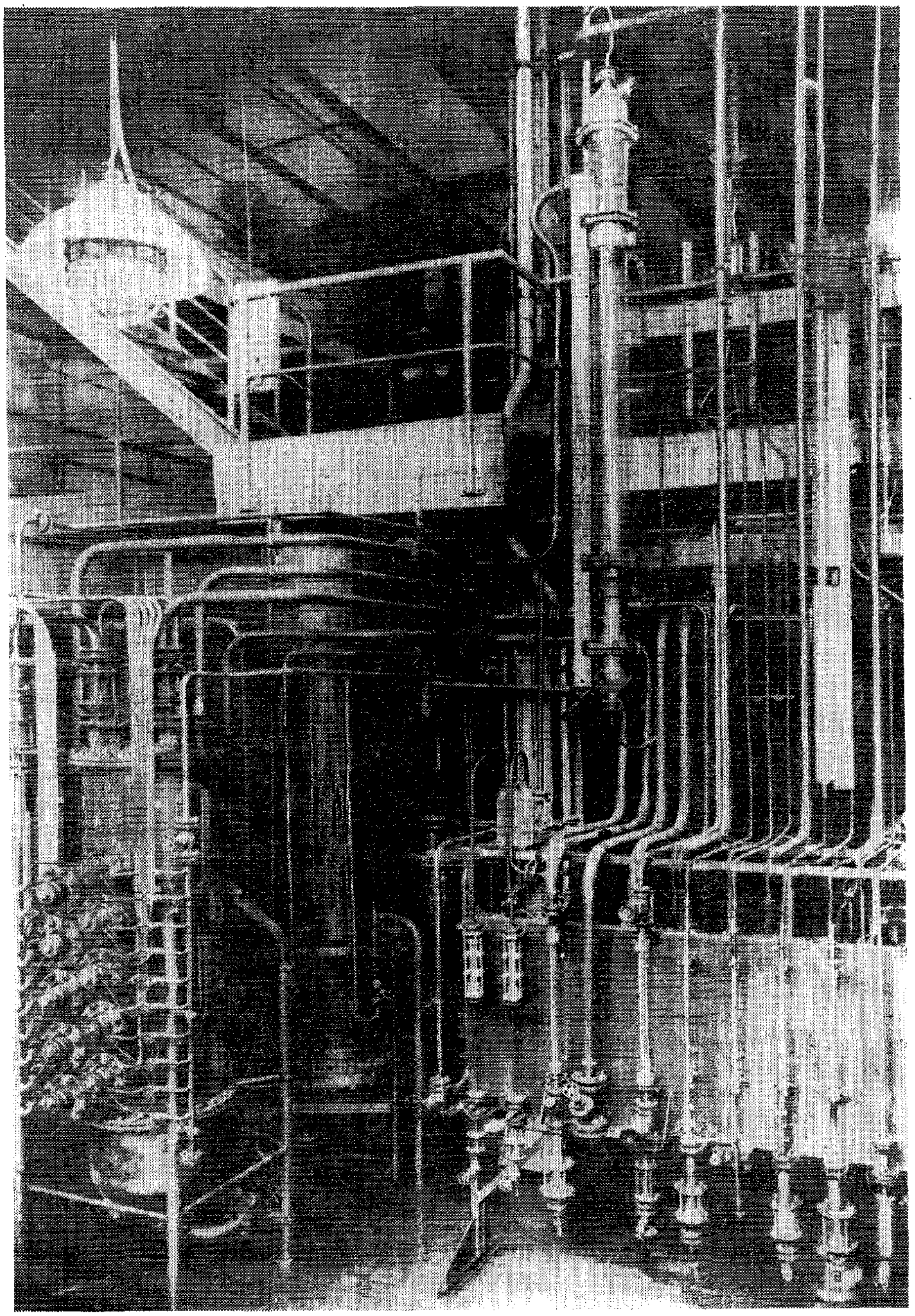


$$RSO_2NH_2 + \frac{R'}{R''}\!>\!C\!<\!\frac{OH}{SO_3M} \longrightarrow RSO_2NHC\!<\!\frac{R'}{R''}\!-SO_3M + H_2O$$

Thus, methyl sulfonamide has been converted to methylsulfonamidomethane sulfonic acid in quantitative yield (*162*). Fatty acid amides are primarily converted into acylaminomethane sulfonic acids (*309*). The latter reaction can be accelerated by addition of an aliphatic, cycloaliphatic and araliphatic secondary amine as a catalyst (*211*). β-Hydroxyalkylamines yield β-hydroxyalkylaminomethane sulfonates (*63*).

UNSATURATED

Olefins may be sulfonated under conditions that either encourage addition of the sulfonating agent to form saturated aliphatic derivatives, or avoid addition, thus preserving the unsaturated character of the molecule. Both methods of sulfonation continue to receive considerable attention.



Sulfochlorination, Sulfoxidation Pilot Plant, I. G. Farbenindustrie, Hoechst

Addition to Give Saturated Compounds. SULFITES AND BISULFITES. The well established method of heating a compound containing a nonbenzenoid double bond with a salt of sulfurous acid in a polar solvent at atmospheric or superatmospheric pressure has been much used to sulfonate complex acids, esters, ethers, ketones, amides, etc. Many of the sulfonates thus produced are commercially valuable emulsifying, wetting, dispersing, deterging, etc., agents and have been patented (*13, 70–72, 81, 88–90, 93, 108, 180, 186–188, 207, 208, 223, 226, 230, 292, 303, 304*). The use of oxidizing agents, such as ascaridole and hydrogen peroxide, is said to promote the sulfonation of *N*-allyl-secondary amines (*190*), as well as acyclic and alicyclic hydrocarbons containing at least six carbon atoms and one double bond (*304*). Preferred conditions for converting polyfluoroethylenes to polyfluoroethane sulfonates involve the use of an oxidizing agent and a buffer such as borax (*15*). Both polymerization and sulfonation occur when an olefin is heated above 400 atmospheres pressure with a salt of sulfurous acid, and this process is promoted by the presence of an oxidizing agent and/or a polyhalogenated hydrocarbon (*137*). Addition of sulfites and bisulfites to acetylene hydrocarbons to form ethylene sulfonate and ethane disulfonate derivatives has been described (*165, 239*). *N*-allyl substituted azo dyestuffs have been solubilized by addition of sulfite to the double bond (*85*).

MISCELLANEOUS. Olefins add sodium chlorosulfonate to form chloroalkyl sulfonates (*302*). Olefin halides containing at least three carbon atoms react with oleum in liquid sulfur dioxide to form a carbyl sulfate derivative (*64*). Sulfuric acid in acetic anhydride reacts at low temperatures to form sulfonates as well as sulfates of the following unsaturated compounds: olefins of high molecular weight (*132, 133*), complex amides (*69*), ethers (*245*), and esters (*25, 131, 171, 218, 222, 246*). Esters derived from aliphatic carboxylic acids and olefinic alcohols yield chiefly sulfonates and sulfates with sulfuric acid, but hydroxysulfonates with chlorosulfonic acid (*194*). Suter *et al.* (*43, 275, 279–283*) studied extensively the sulfonation of olefins with dioxane sulfotrioxide and dioxane chlorosulfonate, and reported that straight-chain α-olefins react with 2 moles of sulfur trioxide by addition to form alkylethionic anhydrides, whereas branched-chain α-olefins undergo this reaction to only a minor extent. A reaction mechanism is discussed (*43*).

Addition or Substitution to Give Unsaturated Compounds. SULFUR TRIOXIDE ADDUCTS. Adducts of sulfur trioxide and an organic or inorganic compound, which contains one or more atoms possessing unshared electron pairs, may also react with olefinic compounds to form unsaturated sulfonic acid derivatives. The reactions of dioxane sulfotrioxide with numerous olefins has been investigated by Suter *et al.* (*43, 275, 279–283*). The behavior of straight-chain α-olefins is noted above. α-Olefins possessing a branch in the chain at the No. 2 carbon atom yield chiefly unsaturated sulfonic acids. This reaction is believed to occur by an additional mechanism (*43*). The sulfonation of tertiary olefins with dioxane sulfotrioxide has been patented (*279*). Thioxane sulfotrioxide has been employed to sulfonate olefinic compounds, and it allegedly offers advantages over other sulfur trioxide—containing adducts (*225, 227*). According to Wolter (*306, 307*) oleyl and other unsaturated alcohols can be sulfonated with the adduct of sulfur trioxide and sodium nitrite without affecting the double bonds of the unsaturated alcohols to form oleyl sulfonate, etc., but the formation of a sulfonate instead of a sulfate is questioned by Groggins (*127*). Sodium chlorosulfonate adds to olefinic compounds to yield chloroalkyl sulfonates, which can be dehydrohalogenated to form unsaturated sulfonates (*302*).

MISCELLANEOUS. Olefin halides react with salts of sulfurous acid by halogen replacement to form unsaturated sulfonates (*43, 76, 77, 80, 282*).

Unsaturated aliphatic mercaptans have been oxidized to unsaturated sulfonic acids (*76*).

Aromatic Compounds

DIRECT SULFONATION

The sulfonic acid group can be readily introduced into most aromatic compounds by employing conventional sulfonating agents—i.e., compounds containing sulfur trioxide. For this reason, direct sulfonation is still the most useful method for obtaining aromatic sulfonic acids.

Monocyclic. The preparation of benzene monosulfonic acid has received considerable attention (*5, 212, 234, 240, 241, 291*). Othmer and Leyes (*234*) found that whereas prior processes use excess sulfonating agent or benzene to drive the reaction to completion, the same effect can be obtained by reacting stoichiometric amounts of benzene and sulfuric acid in an inert high boiling solvent, while removing water, present and formed, by azeotropic distillation. (It would seem that the contamination and material losses resulting from charring of the high boiling diluent as well as decreased batch size at least partly offset the advantages claimed—viz., avoidance of sulfone formation and use of excess sulfuric acid.)

Maguire and Gould (*212*) patented an improved process for preparing benzene monosulfonic acid. Benzene vapors are passed into sulfuric acid in excess of the requirement for the reaction in order to remove the water present and formed, whereby less than 10% of unreacted sulfuric acid remains and less than 2% of diphenyl sulfone is formed. Accordingly, this process is claimed to be superior to those patented by Tyrer (*291*) and Ambler (*5*). Planovskiĭ and Kagan (*240, 241*) present a comprehensive review, classification, and evaluation of a number of batch and continuous methods for the production of benzene monosulfonic acid, especially with respect to material and energy consumption as well as equipment requirements. These authors concluded that the economically most attractive processes involve sulfonation of benzene with gaseous sulfur trioxide, or benzene vapors with sulfuric acid, in a continuous manner. These processes are discussed in greater detail under continuous technical methods below. Liquid sulfur dioxide has been employed as a solvent for the sulfonation of benzene (*256*). Benzenesulfonic acid or diphenyl sulfone is obtained as the principal product, depending on the temperature, when a mixture of sulfuric acid and hydrogen fluoride reacts with benzene (*270*). Hennion (*149*) patented the use of boron trifluoride as an advantageous catalyst for sulfonating benzene and its derivatives to give nearly theoretical yields of the corresponding sulfonic acids.

The azeotropic distillation method noted above has been applied to the sulfonation of toluene (*52*) and aniline (*179*) to produce the corresponding monosulfonic acids. In the case of aniline an inert high boiling solvent was used, and optimum yields (95.7% of theory) of sulfanilic acid were obtained by employing stoichiometric amounts of acid and aniline, and distilling off only the theoretical amount of water.

The sulfonation of monoethylaniline is analogous to that of monomethylaniline: with 20% oleum, *p*-monoethylanilinesulfonic acid is the main product at 185° to 190° C., whereas the *m*- isomer together with some *p*- isomer results at a temperature below 60° C. (*267*). Woodruff (*308*) reported that acetophenone and chlorosulfonic acid, when mixed cold and heated, forms acetophenone 2-α-disulfonyl chloride, whereas addition of acetophenone to chlorosulfonic acid at 170° C. gives the corresponding 3- isomer. Similarly, the order of mixing determines the nature of the reaction product in the sulfonation of dimethylaniline with chlorosulfonic acid. Thus, the anhydro salt is exclusively formed when the base is added to the acid, whereas the reverse order produces *p*-dimethylaminobenzenesulfonic acid as well as the anhydro salt (*173*).

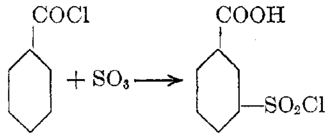
Alexander (*2*) studied the mechanism of sulfonation of aromatic amines. He found that in the sulfonation of aniline with oleum at 10° to 95° C., the ratio of *m*- to combined *o*- and *p*-monosulfonic acids is always less than 1. He reviewed the previous knowledge that the reaction of dimethylaniline with oleum yields the *m*-sulfonic acid exclusively at 55° to 60° C. but the *p*- isomer at 180° C. (baking process), a behavior shared by aniline at the higher temperature. He attributed *p*-sulfonation to the formation of a molecular complex addition product between the base and sulfur trioxide. The absence of a dimethylaniline complex at lower temperatures was indicated by freezing point data, thus accounting for exclusive *m*-sulfonation.

Blangey *et al.* (*36*) identified several isomeric compounds in a study of the sulfonation of ethylbenzylaniline. They found that ethylbenzylaniline-*m*-sulfonic acid was formed when oleum or excess chlorosulfonic acid was used, whereas ethylbenzylaniline-*p*-sulfonic acid resulted when the stoichiometric amount of chlorosulfonic acid in nitrobenzene was employed, or the sulfuric acid salt of the base was baked.

Moser (*220*) states that direct sulfonation of anthranilic acid results in decarboxylation, whereas baking of the acid sulfate gives 1-aminobenzene-4-sulfo-2-carboxylic acid in nearly quantitative yield.

Ruggli and Stäuble (*259*) studied the sulfonation of a number of polyazobenzenes with oleum and found that these compounds are first sulfonated in the *p*- positions of the end nuclei, and then in the intermediate nuclei.

Meiser (*215*) patented the method of sulfonating aromatic carboxylic acid chlorides with sulfur trioxide to yield the corresponding sulfonyl chloride derivatives of the carboxylic acids:



α-Methylstyrene reacts with 96% sulfuric acid to form a mixture of *m*- and *p*-sulfonated isomers (*57*).

Polycyclic. Numerous recent publications attest to continued interest in the sulfonation products of naphthalene, and improved methods for their production (*99, 196, 197, 199, 200, 225, 233, 271, 272*). Othmer *et al.* (*233*) found that naphthalene monosulfonic acids can be obtained in 96% yield by the reaction of naphthalene and sulfuric acid at 160° C. in an inert solvent while water is removed by azeotropic distillation. Spryskov's (*271, 272*) study of the monosulfonation of naphthalene is reported below under a discussion of mechanism. Lantz (*196, 197, 199, 200*) investigated the sulfonation of naphthalene and sulfonation and desulfonation of naphthalene mono-, di-, and trisulfonic acids. He found that the velocity of introduction or elimination of a sulfonic acid group is greater in the alpha than in the beta position, and is diminished by the presence of a sulfonic acid group in the other ring, the diminution of the velocity of introduction being less when the latter group is in the beta position, but its position having little influence on the velocity of elimination.

Fierz-David and Richter (*99*) state that mono- and disulfonation of naphthalene are rapid exothermic reactions, whereas the tri- and tetrasulfonation reactions are endothermic processes. Moreover, the ease of introduction of further sulfo groups decreases with increasing degree of sulfonation. These authors identified all six of the disulfonic acids predicted by the rule of Armstrong-Wynne in the reaction mass obtained in the disulfonation of naphthalene with 100% sulfuric acid at 130° C. It is of interest to note that 1-naphthalene monosulfonic acid can be obtained by the reaction of naphthalene with thioxane sulfotrioxide, whereas this sulfonating agent does not react with benzene under the same conditions, and is thus distinguished from dioxane sulfotrioxide, which sulfonates both naphthalene and benzene (*225*, *278*).

Shreve and Lux (*269*) investigated the monosulfonation of 2-methylnaphthalene at various temperatures and found that the sulfonic acid group enters the 8- position at 40° C., the 6- position at 90° to 95° C., and the 7- position at 160° C.

Vorontsov *et al.* (*294*) state that the following reactions occur during sulfonation of 2-naphthol with 2.7 mole equivalents of 92% sulfuric acid at 50° to 55° C. up to 60 hours: sulfonation to 2,1-, 2,8-, 2,7-, and 2,6-naphtholsulfonic acids; desulfonation of 2,1- and 2,8-naphtholsulfonic acids; sulfonation of 2,8-naphtholsulfonic acid to 2,1,6- and 2,6,8-naphtholdisulfonic acids; and desulfonation of 2,1,6-naphtholdisulfonic acid.

Sulfonation of 1- and 2-napthylamine and 2-naphthol may be effected at a lower temperature and results in reaction products of purer quality where boron trifluoride is used with concentrated sulfuric acid as the sulfonating agent. The role of boron trifluoride is that of a dehydrating catalyst, the ratio of isomers remaining unchanged (*150*). Hennion (*149*) patented the use of boron trifluoride as an advantageous catalyst in the sulfonation of numerous naphthalene and other compounds.

Arnold and Zaugg (*7*) obtained a mixture of 4- and 5-hydrindene sulfonyl chlorides in 76% yield by adding hydrindine to chlorosulfonic acid below −10° C. After separating the mixture by fractional distillation, the 4- isomer was hydrolyzed to give sodium hydrindine-4-sulfonate in 81% yield.

Ioffe (*172*) reacted phenanthrene and sulfuric acid at 110° to 120° C. and obtained the 2- and 3-monosulfonic acids. The reaction of 9-bromophenanthrene and sulfuric acid at about 100° C. yields a mixture of the corresponding 2- and 3-monosulfonic acids (*214*). Retene (1-methyl-7-isopropylphenanthrene) reacts with an equal weight of sulfuric acid at 185° to 190° C. to form the 6-sulfonic acid in 73 to 75% yield (*184*). Cromwell and Merley (*66*) patented an improved method for sulfonating abietic acid and related compounds, which comprises treating them with pyrosulfuryl chloride at a temperature below −10° F. According to another patented process, the sulfonation of rosin (90% abietic acid) is effected with oleum in a low boiling solvent, such as liquid sulfur dioxide, and in the presence of a catalyst, such as aluminum borate or zinc chloride (*120*).

3-Aminopyrene-4-sulfonic acid, which is an intermediate for the valuable coupling component 3-hydroxypyrene, can be obtained by baking the acid sulfate of 3-aminopyrene (*73*).

Ogilvie and Hoare (*231*, *232*) describe the sulfonation of 1-aminoanthraquinone by heating an intermediate compound thereof with chlorosulfonic acid either alone or in concentrated sulfuric acid to give nearly theoretical yields of the 2-sulfonic acid.

Ioffe *et al.* studied the sulfonation of 1,2-benzanthraquinone with sulfuric acid and oleum under various conditions, and found that the 2′- and 4′-monosulfonic acids were formed, the former predominating under mild conditions (*174*, *175*). 1,9-Benzanthrone can be sulfonated under ordinary conditions to give only the 6-sulfonic acid; the less stable 1′-sulfonic acid is obtained by sulfonation with an equivalent amount of chlorosulfonic acid in ethylene dichloride, and it may be readily transformed into the 6-sulfonic acid in acid solution; the 1′,6-disulfonic acid results from the reaction of 1,9-benzanthrone with oleum, or on further sulfonation of the 1′- and 6-monosulfonic acids (*178*). Violanthrone and its 2,2′-dihydroxy derivative, when treated with 100% sulfuric acid at 100° C. or with 20% oleum at 20° C., yield the corresponding 6,6′-disulfonic acids (*176*).

Aliphatic-Aromatic Compounds. Sustained commercial interest in long-chain alkyl aromatic sulfonates is evident from the patent literature. Many of these sulfonate products are complex mixtures of compounds, which are derived chiefly from petroleum and coal-tar fractions, and which possess valuable wetting and deterging properties. Numerous patents disclose the formation of alkyl aromatic sulfonic acids by direct sulfonation of alkyl aromatic compounds (*45*, *46*, *48*, *50*, *100–107*, *109–115*, *124*, *140*, *167*, *191–193*, *205*, *216*, *217*, *224*, *230*, *242*, *251*, *274*, *287*, *290*, *296*, *300*). An alternative method for preparing such products involves combining the condensation and sulfonation operations in a single step—e.g., reaction of an aliphatic alcohol, olefin, etc., with an aromatic compound and an agent, which functions in both a condensing and sulfonating capacity (*47*, *53*, *119*, *141*, *145*, *166*, *217*, *224*, *230*, *247*, *301*, *311*).

Liquid sulfur dioxide is stated to be an advantageous medium for effecting sulfonation or combined condensation and sulfonation reactions, as it avoids polymerization, oxidation, charring, and other side reactions, and can also be used to provide close control of reaction temperatures (*45–50*, *68*). In addition, use of liquid sulfur dioxide in a closed system permits economical operation (*47*). The condensation and sulfonation operations may be effected advantageously by treating an olefin and an aromatic compound with sulfuric acid in an amount insufficient to complete the reaction, separating the aqueous phase, and treating the unreacted portion with fresh sulfuric acid as before. In this manner, a 98% yield of tetraisobutylphenol sulfonate was obtained (*53*). An improved process for preparing alkylaryl sulfonates involves reacting an aliphatic hydroxy compound containing more than eight carbon atoms and an aromatic hydrocarbon with a mixture of sulfuric acid and sodium pyrosulfate. This mixture is more effective than sulfuric acid alone, and avoids the dark colored products obtained when oleum is used (*311*).

INDIRECT SULFONATION

The reaction of salts of sulfurous acid on aromatic compounds containing halogeno, nitro, nitroso, hydroxyl, and carbonyl substituents has found limited use for preparing aromatic sulfonic acids. Recent contributions have been along already developed lines. *m*-Nitrotoluene and aqueous sodium bisulfite yield *m*-tolylsulfamic acid together with a small amount of *p*-sulfo-*m*-tolylsulfamic acid (*41*). Bogdanov (*40*) found that *p*-nitrotoluene reacts with aqueous sodium bisulfite in the presence of 2-naphthol to form *p*-toluenesulfamic acid and 2-naphthol-1-sulfonic acid, yields of products decreasing with increasing pH. He also studied the effect of substituted aromatic hydroxycompounds on the reaction of bisulfites and aromatic nitro compounds, and found that some substituted aromatic hydroxy compounds such as 2-hydroxy-3-naphthoic acid, 2-naphthol-4-sulfonic acid, and hydroquinone, hinder the reaction, whereas others do not—e.g., phenol, 2-naphthol-1,4-disulfonic acid, 1-sulfo-2-hydroxy-3-naphthoic acid, hydroquinone disulfonic acid, and 3,6-dichlorohydroquinone disulfonic acid. In this connection he observed that the aromatic hydroxy compounds could be sulfonated to a small extent by passing air through an aqueous solution of sodium bisulfite and the aromatic hydroxy body in the absence of the aromatic nitro compound (*42*). Pearl (*204*, *238*) patented a procedure for synthesizing *p*-azobenzene sulfonic acid from nitrobenzene and sulfite waste liquor. *o*-Sulfobenzoic acids can be obtained in good yield by heating the corresponding *o*-halogenobenzoic acid and an aqueous inorganic sulfite solution in the presence of a copper catalyst (*273*). In the anthraquinone series, the sulfite reaction has been applied to replace the 2-halogen atom of 4-substituted 1-amino-2-halogenoanthraquinones (*142*).

In addition to its normal behavior as an esterifying agent, dimethyl sulfate may function as a sulfonating agent. At high temperatures, traces of water form methyl hydrogen sulfate, which tends to form ammonium salts with aromatic amines; but when this reaction is difficult, as with *N*-methyldiphenylamine and triphenylamine, sulfonation of the aromatic ring also occurs (*22*). Sulfonic acids can also be formed by the reaction of dimethyl sulfate with aromatic ethers, such as anisole, diphenyl

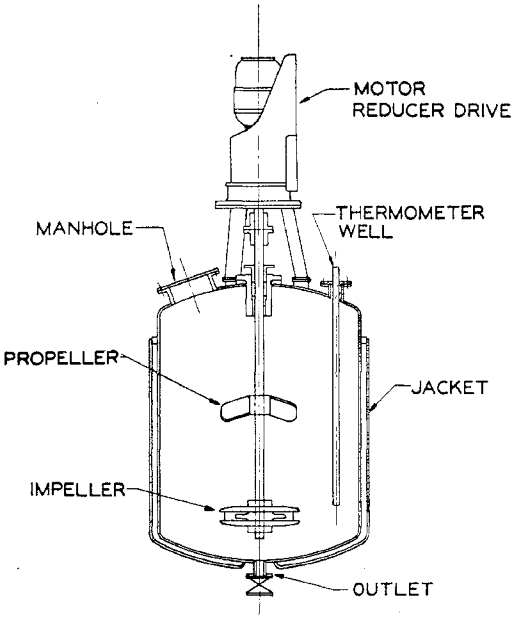


Figure 1. Batch Sulfonator

ether, and 2-methoxynaphthalene; but no sulfonation occurs in the case of purely aliphatic ethers, or aromatic ethers wherein the aromatic nucleus is remote from the ether linkage—e.g., diisoamyl ether and benzyl methyl ether (*23*).

N-alkyl sulfonic acids of the anthraquinone series can be prepared by an improved process, wherein a primary aminoanthraquinone is reacted with an aliphatic aldehyde bisulfite in the presence of an organic solvent, such as alcohol, phenol, and benzene (*261*). McIlwain prepared α-aminophenylmethane sulfonic acid by reaction of benzaldehyde and aqueous ammonium sulfite (*210*).

The sulfonation of lignin by sulfite treatment has been reviewed (*91*) and it has been further studied, particularly with regard to the mechanism of the reaction (*92, 262*).

Heterocyclic

Erlenmeyer and Kiefer (*94*) discovered that thiazole, and 2-substituted thiazoles, yield the corresponding 5-sulfonic acids when reacted with oleum in the presence of mercuric sulfate. They also prepared 4-thiazolesulfonic acid by similar sulfonation of 2,5-dibromothiazole followed by dehalogenation of the resulting 2,5-dibromo-4-thiazolesulfonic acid. McElvain and Goese (*209*) determined the optimum conditions for sulfonating pyridine and α-, β-, and γ-picolines. In every case, the sulfonic acid group entered the 3- position and the yield of sulfonate depended on at least three factors: (1) presence of mercuric sulfate in catalytic amounts; (2) presence of one equivalent of sulfur trioxide in the oleum used in sulfonation; and (3) time of reaction at 220° to 230° C. Rogers (*253, 254*) obtained novel disulfonic acid derivatives by sulfonating di- and triphenylpyrroles with oleum.

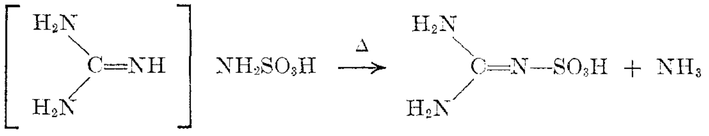
Ioffe and Khavin (*177*) discovered that 1-phenyl-3-methyl-5-pyrazolone yields the 4-sulfonic acid derivative when treated with 100% sulfuric acid at a temperature below 10° C., whereas the 4′-sulfonic acid is obtained at higher temperatures.

According to Hennion (*149*) heterocyclic compounds may be advantageously sulfonated with sulfuric acid by using boron trifluoride as a catalyst.

Tiesler (*289*) discloses a commercially attractive method for obtaining 4-pyridine sulfonic acid, which comprises heating 4-pyridylpyridinium chloride with sodium sulfite or bisulfite in aqueous solution.

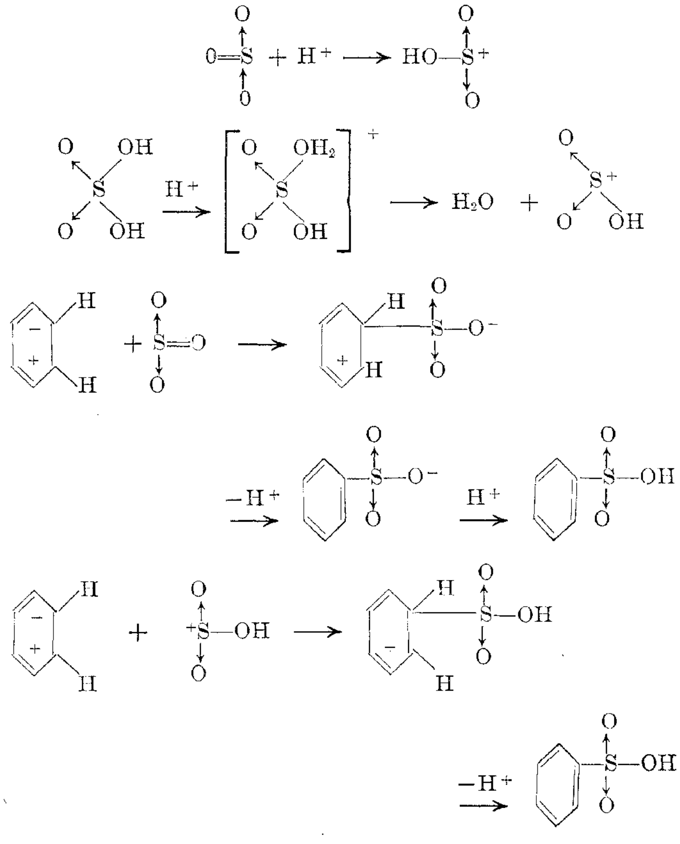
Huppert (*157*) states that 3,5-disubstituted thiohydantoin-2-sulfonic acids can be formed by oxidation of the corresponding disulfides with hydrogen peroxide or halogen.

Hill (*152*) patented a unique method for synthesizing guanidinesulfonic acid, which comprises heating guanidine sulfamate to spilt out ammonia:

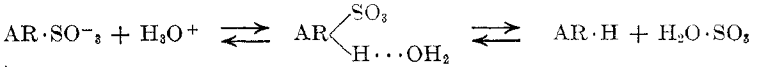


Mechanism

Numerous theories have been proposed to explain the mechanism of aromatic sulfonation with compounds containing sulfur trioxide. It has been explained on the basis of a cationoid mechanism (*244, 284*) involving the electrophilic sulfur trioxide, which may react in the form of an ion such as HO_3S^+ or SO_3 itself, attacking the negative center of a polarized form of the hydrocarbon. It is assumed in the case of sulfuric acid that dissociation occurs in such a way as to lose a hydroxyl group. Such a mechanism may be illustrated in the following manner:

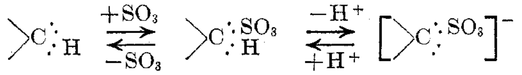


From kinetic studies, Baddeley, Holt, and Kenner (*14*) concluded that desulfonation of substituted benzenesulfonic acids should not be regarded as one of hydrolysis, inasmuch as the anion rather than the acid is involved. They found that when the desulfonation is carried out in 90% acetic acid containing an inorganic acid, the reaction rate is independent of the concentration of the sulfonic acid and the inorganic anion, but is proportional to the hydrogen ion activity according to the first-order equation. They conceived that a reversible relationship between desulfonation and sulfonation exists as follows:



$$AR\cdot SO_3^- + H_3O^+ \rightleftharpoons AR\begin{matrix}SO_3\\ H\cdots OH_2\end{matrix} \rightleftharpoons AR\cdot H + H_2O\cdot SO_3$$

According to Baddeley, Holt, and Kenner, sulfonation involves $H_2O\cdot SO_3$ rather than $SO_2\cdot(OH)_2$. [In this connection Baumgarten (*16*) has shown experimentally that available sulfur trioxide is present in concentrated sulfuric acid. Incidentally, this information is part of an excellent review of the chemistry of sulfur trioxide and its adducts with compounds containing atoms having unshared electron pairs, in which reactivity is explained on the basis of constitution.] Water aids sulfonation by removal of a proton from the transition complex, whereas the fact that the sulfonate ion carries a negative charge facilitates desulfonation. The lack of such a charge commonly inhibits reversibility in other substitution reactions. These views are in accord with the work of Lantz (*198*), who proposed that in sulfonation the reaction mechanism involves as a first step the fixation of the electrophilic sulfur atom of sulfur trioxide to an atom containing an unshared electron pair—nitrogen of a tertiary amine, oxygen in dioxane, and carbon of an aromatic hydrocarbon—whereas in desulfonation a proton is first contributed by a strong acid, such as sulfuric or pyrosulfuric acid, to form an unstable intermediate. The second step consists in the elimination of sulfur trioxide for desulfonation, and a proton for sulfonation. This mechanism may be visualized in the following way (wherein $\rangle C \vdots_{H}$ represents the reactive form of a carbon atom of an aromatic nucleus and H^+ is indicated in place of a proton donor):



$$\rangle C\vdots H \underset{-SO_3}{\overset{+SO_3}{\rightleftarrows}} \rangle C\vdots^{SO_3}_{H} \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} \left[\rangle C\vdots^{SO_3}\right]^-$$

Bradford and Jones (*44*) reviewed the influence of substituents on the rate of sulfonation of various monosubstituted benzene compounds as well as their effect on the activation energies of the reactions. Hinshelwood *et al.* (*83, 295*) investigated the kinetics of the sulfonation of nitrobenzene and seven substituted derivatives (in nitrobenzene) with sulfur trioxide, and found that the reactions were second order with respect to sulfur trioxide, first order with respect to the aromatic compound, and retarded by formation of the product in every case. A tentative mechanism was proposed whereby the dimeric form of sulfur trioxide, S_2O_6 was considered to be the active species according to the scheme:

$$2SO_3 \rightleftarrows S_2O_6$$

$$ARH + S_2O_6 \longrightarrow ARS_2O_6H$$

$$ARS_2O_6H \rightleftarrows ARSO_3H + SO_3$$

The effects of substituents in the benzene ring on the rate of sulfonation were explained by changes in activation energy, and a correlation was established between such changes and the electronic effects of substituents, as measured by dipole moments for all compounds except *p*-nitroanisole. It was pointed out that additional data are necessary before any far-reaching conclusions can be made. Values are shown in Table I.

Table I. Effect of Substituents in Benzene Ring

	Velocity Constant (L./G.-Mol. Sec.), *k* 40°	Activation Energy (Cals./G.-Mol.), *E*	Dipole Moment Functions' $f(\mu)$
Benzene	48.8 (40.8)	4800 (5500)	0.00
Chlorobenzene	2.4	7720	1.56
Bromobenzene	2.1	7840	1.53
m-Dichlorobenzene	4.36×10^{-2}	9220	3.12
Nitrobenzene	7.85×10^{-6}	11400	3.97
p-Nitrotoluene	9.53×10^{-4}	11025	3.56
p-Nitroanisole	6.29	4320	..
α-Nitronaphthalene	3.27	7900	..

Suter *et al.* (*43*) investigated the reaction of dioxane sulfotrioxide on various types of olefins and other unsaturated compounds and proposed a mechanism for the reaction, which accounts for both saturated and unsaturated sulfonation products (see above).

Lantz (*196, 197, 199, 200*) conducted an intensive study of the kinetics of sulfonation of naphthalene and sulfonation and desulfonation of naphthalene mono-, di-, and trisulfonic acids. This work among others was reviewed by Hodgson and Hathway (*153*) in a theoretical discussion of positional sulfonation of naphthalene and some of its derivatives based on the modern resonance theory. Contributions to the knowledge of sulfonation of naphthalene by Fierz-David and Richter (*99*) were also discussed in the same connection. In a second similar review paper concerning the sulfonation of 1- and 2-naphthols, 1- and 2-naphthylamines and their common monosulfonic acids, Hodgson and Hathway (*154*) consider in some detail the recent work of Alexander (*2*) on the mechanism of the sulfonation of aromatic amines (see above).

The generally accepted concept of π-sulfonation—i.e., minimum concentration of sulfuric acid necessary for sulfonation, depending only on temperature and compound to be sulfonated (*127*)—has been challenged by Spryskov (*271, 272*). This investigator showed experimentally that the end concentration of sulfuric acid depends not merely on the sulfonation temperature and the compound sulfonated but also on the amount of said compound as well as the initial strength and amount of the sulfuric acid and time of reaction. He monosulfonated naphthalene with sulfuric acid to give spent acid concentrations as low as 40.3% at 100° C. and 25% at 162° C., which are far below values of 65 and 63.7%, respectively, previously established (*65, 134*). Spryskov deduced that an equilibrium condition exists not only for the sulfonation and desulfonation reactions

$$C_{10}H_8 + H_2SO_4 \rightleftarrows C_{10}H_7SO_3H + H_2O$$

but also between the water present, or formed, and the sulfuric and sulfonic acids:

$$H_2SO_4 + H_2O \rightleftarrows H_2SO_4\cdot H_2O$$

$$H_2SO_4\cdot H_2O + H_2O \rightleftarrows H_2SO_4\cdot 2\ H_2O$$

$$C_{10}H_7SO_3H + H_2O \rightleftarrows C_{10}H_7SO_3H\cdot H_2O$$

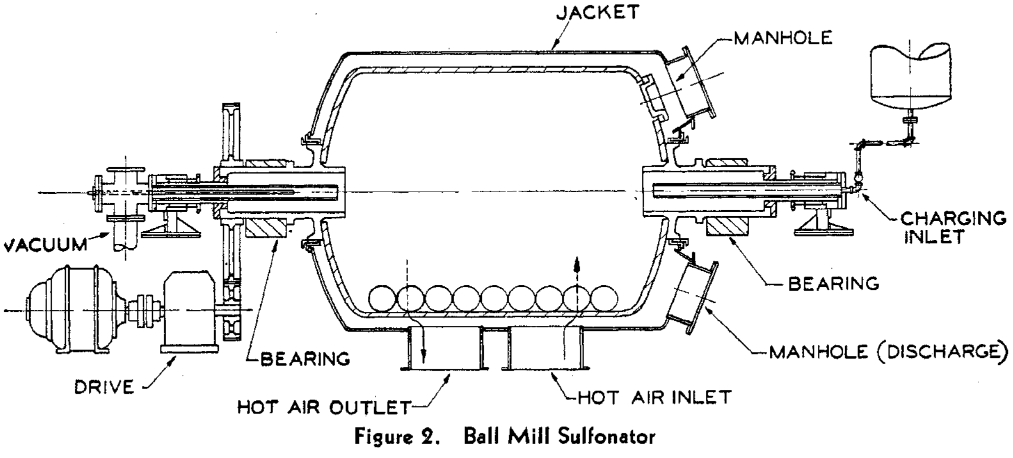


Figure 2. Ball Mill Sulfonator

Identification and Analysis of Sulfonic Acids

In recent studies, the customary method employed for identification of sulfonic acids by formation of a derivative possessing a suitable melting point has been extended. The following derivatives of sulfonic acids have been formed: *S*-benzylthiuronium salts (*60, 118*); *p*-nitrobenzylpyridinium salts (*156*), arylamine salts (*75*), and thallous salts (*122*). Amino-substituted aromatic sulfonic acids have been identified by conversion to a sulfonyl chloride, amide, or anilide of the corresponding halogen-substituted sulfonic acids (*3*). Arylamine salts have been used to separate naphthalenesulfonic acids. This is a particularly useful method for quantitative estimation of aliphatic and aromatic sulfonic acids, because the isolated salt can be titrated with standard alkali (*213, 310*). Thallous hydroxide and formate have been suggested for separation and isolation of isomeric sulfonic acids (*122*). A bromination method has been reported for quantitative determination of isomeric aminobenzene sulfonic acids (*266*). Naphthalene mono-, di-, and trisulfonic acids and mixtures thereof have been assayed by a method involving nitration and sulfonation (*195*). Sulfonated or sulfated surface-active compounds may be quantitatively estimated by a colorimetric method involving the formation of a colored salt with methylene blue (*183*).

TECHNICAL DEVELOPMENTS

Until recently the principal source of information concerning commercial sulfonation methods has been the patent literature. At the present this source is augmented by numerous governmental reports—e.g., FIAT, BIOS—describing, among others, German chemical industrial operations.

Methods

Commercial sulfonation methods are treated in this paper under separate headings: batch and continuous processing. Batch methods still predominate, and it is evident from BIOS and similar reports that such methods were employed almost exclusively by the German chemical industry (*27–29, 33, 73, 97, 98, 170*). However, continuous sulfonation has found increasing application to the manufacture of large poundage products—e.g., organic sulfonates possessing wetting and detergent properties (*26, 31, 34, 46–48, 221*), benzenemonosulfonic acid (*240, 241*), and 2-naphthalenesulfonic acid (*73*). Although continuous operation generally provides increased production capacity and permits improved process control and quality of product, it entails higher process development costs, larger capital expenditure for equipment, and need for more highly skilled operators. Such costs and requirements are ordinarily prohibitive. However, continuous operation permits a substantially lower unit cost when production levels are sufficiently high, as in the manufacture of widely used synthetic organic sulfonate detergents, and thus can overcome the aforesaid disadvantages.

BATCH PROCESSING

Methods. Perhaps the richest source of information concerning methods for manufacturing organic sulfonic acids has appeared in BIOS and similar reports on the German chemical industry, which often disclose valuable information on types of equipment, power, labor, and other requirements. Some of the more important references for the following classes of sulfonic acids are noted: aliphatic sulfonic acids (*34, 97*), monocyclic aromatic sulfonic acids (*27, 29, 30, 32, 33, 98*), and polycyclic aromatic sulfonic acids (*27, 28, 98*).

The partial pressure distillation method has been applied to promote the batch sulfonation of aromatic compounds with sulfuric acid: benzene to benzenemonosulfonic acid (*234*), toluene to *p*-toluenemonosulfonic acid (*52*), aniline to sulfanilic acid (*179*), naphthalene to naphthalenemonosulfonic acids (*233*), 4-phenetidine to 4-phenetidine-3-sulfonic acid (*29*), 4-aminobiphenyl to 4-aminobiphenyl-3-sulfonic acid (*98*), and others. This method is commercially attractive, as it drives the reaction to completion by removal of water by azeotropic distillation, and thereby permits the use of stoichiometric amounts of reactants, and it may also avoid the formation of undesirable isomers. Thus, *p*-toluenesulfonic acid together with only 2 to 5% of the *m*-isomer is obtained by subject method, whereas considerably larger amounts of the *m*- isomer are formed by other methods (*52*). This technique has been applied commercially to the manufacture of *o*-sulfonic acid derivatives of aromatic amines. Thus, 4-phenetidine-3-sulfonic acid can be obtained in 93% yield, and 2-(4′-aminophenyl)-6-methylbenzthiazole-3′,7-disulfonic acid is produced in 94.5% yield by heating the corresponding aromatic amine with sulfuric acid in "ortho oil" [technical *o*-dichlorobenzene (*29*)].

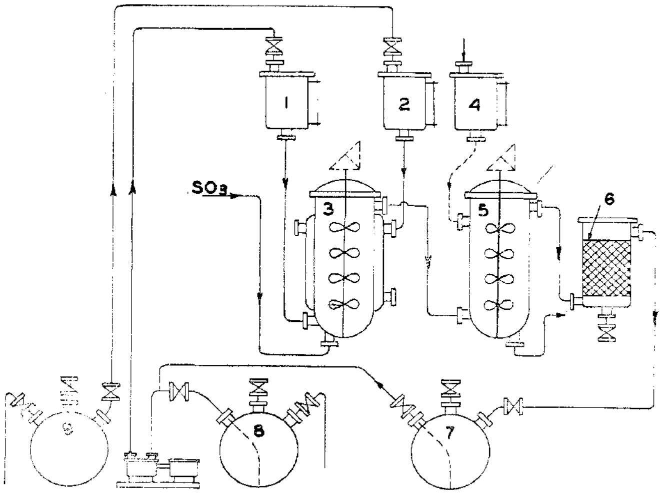


Figure 3. Flow Diagram of Continuous Sulfonation

Hennion (*149, 150*) patented an improved process for sulfonating organic compounds, which comprises reacting a mixture of sulfuric acid and an inorganic compound of the aromatic or heterocyclic series in the presence of at least 0.05 mole equivalent of boron trifluoride. The process is said to provide a shorter reaction period and improved yield and quality of sulfonate product. In addition, only the stoichiometric quantities of reactants are required, and the catalyst may be easily separated and recovered.

Nawiasky and Sprenger (*225, 227*) describe an adduct of sulfur trioxide and thioxane, as a new sulfonating agent. This agent is said to possess greater commercial utility than other sulfur trioxide adducts derived from pyridine, dialkyl ethers, dioxanes, etc., especially in that it permits sulfonating olefins by substitution, and the residual uncombined thioxane may be more readily recovered from the sulfonation mass than dioxane or pyridine.

Special forms of sulfuric anhydride, which have recently appeared on the market, are of potential interest as commercial sulfonating agents: Sulfan A, a partially stabilized product, consisting largely of β-sulfur trioxide and melting at 30–35° C.; Sulfan B, a completely stabilized product, consisting largely of γ-sulfur trioxide and melting at 17° C.; and Sulfan C, an unstabilized sulfur trioxide, which will eventually polymerize to α-sulfur trioxide (*121*).

Numerous other references disclosing batch sulfonation methods and/or sulfonate products of technical interest are disclosed above. To avoid undue repetition, they are not included here.

Apparatus. Perhaps this field can best be summarized by a statement made on August 1, 1946, by Boehme, director of intermediates manufacture, I. G. Farbenindustrie, Leverkusen, that since 1937 no new developments had occurred in the design of apparatus for special purposes, such as thick sulfonation or nitration reaction masses (*33*).

Two types of batch sulfonators which find general application in the organic chemical industry and, in particular, in the manufacture of dyestuff intermediates, are illustrated in Figures 1 and 2.

These sulfonators usually vary in capacity from less than 100 to about 800 gallons. Two common types of agitators, propeller and impeller, are used as shown in Figure 1; another common style is the anchor (horseshoe) agitator. The majority of sulfonators used at I. G. Farbenindustrie, Leverkusen, were of approximately 400- or 800-gallon capacity and each was provided with a close fitting anchor agitator carrying two additional vertical arms; the blades had a knife-edge on the leading side to facilitate agitation of thick masses. A battery of seven or eight sulfonators was belt-driven from a common shaft operated by a 100-h.p. motor (*29*).

Ball mill sulfonators, as illustrated in Figure 2, are used principally to carry out sulfonations that give rise to solid, doughy, or thick masses not readily stirrable in the conventional batch sulfonators discussed above, such as in the manufacture of naphthionic acid from 1-naphthylamine, sulfanilic acid from aniline, and 2-naphthol-6-sulfonic acid from 2-naphthol (*28*).

CONTINUOUS PROCESSING

A fundamental advantage of continuous over batch processing is higher capacity per unit volume of reactor. This is generally achieved by increasing the rate of reaction—raising the temperature, increasing the efficiency of agitation, or using a more vigorous sulfonating agent—although it may be attained by other means, such as changing the ratio of reactants.

Planovskiĭ and Kagan (*241*) describe the following continuous process for preparing benzenemonosulfonic acid, which incorporates the advantages but not the disadvantages of two prior processes discussed below.

A sulfonator-extractor, 3 (flow diagram illustrated in Figure 3) is filled to 40 to 60% of capacity with 100% sulfuric acid from tank 9 via measuring tank 2. Benzene is continuously introduced from tank 1 under pressure into the sulfonator, which is intensively agitated to provide a state emulsion for the energetic reaction. In the upper part of the sulfonator, a layer of benzene containing dissolved benzenemonosulfonic acid separates and overflows into an extractor, 5. Sulfur trioxide is introduced continuously into the sulfonator so as to react with the water generated in the reaction and thus maintain the acid concentration at 100%. In extractor 5 the benzenemonosulfonic acid is extracted continuously from the benzene with water or sodium hydroxide solution introduced from tank 4 and is continuously separated and discharged at the bottom of the extractor while the benzene passes from the top of the extractor to a dryer, 6, and is recycled via tanks 7 and 8 by pump to storage tank 1.

Table II. Process for Benzene Monosulfonic Acid

Process Description	Kg. of Sulfonating Agent Consumed/ Kg. of Benzene	No. of Cycles of Benzene	Heat Balance, Cal.	Cubic Contents of Sulfonator, Cu. M.	Sulfones, %
Excess acid (classical method), batch	1580	1	+214,000	1.4	<2
Dennis-Bull, continuous	1260	20–30	−70,000	3.7	<2
Gaseous sulfur trioxide, continuous	1260	1	+106,000	Tube diam. = 1200 mm. height = 5000 mm.	30
Extraction-sulfonation, continuous (see above)	1260	10–20	+106,000	0.37	<2

As shown in Table II, the Planovskiĭ and Kagan process thus described eliminates the excess sulfone formation attending the sulfonation of benzene with gaseous sulfur trioxide, while avoiding the high caloric requirement and large reaction volume of the Dennis and Bull continuous sulfonation-extraction process (*54, 74*).

Planovskiĭ and Kagan (*240*) have also adapted the vapor phase batch processes described by Guyot (*134*), Tyrer (*291*), and more recently by Maguire and Gould (*212*) to an efficient continuous process for monosulfonating benzene. The process is performed as illustrated in the flow diagram, Figure 4.

Sulfuric acid is continuously pumped from storage tank 1 by means of pump 2 through pressure regulator 3 and meter 4 to the sulfonator, 5. Liquid benzene from storage tank 6 or 14 is continuously fed by pump 7 through meter 8 to the direct vaporizer-superheater, 9, and thence to sulfonator 5 and sulfonation tower 10. In the sulfonator sulfuric acid reacts with benzene, and the reaction mass containing 30% unreacted sulfuric acid flows out continuously to the top of tower-sulfonator 10, which is arranged like a plate column. The reaction mass flows downwardly through the tower while further reacting with a countercurrent stream of benzene vapors. The exit benzene-water vapors are continuously discharged from the top of tower 10 to condenser 11, and stratified in separator 12, and the benzene is returned through neutralizing dryer 13 to benzene storage 14, while the benzenemonosulfonic acid containing 2.5 to 3.5% of sulfones and 3 to 4% of sulfuric acid is continuously drawn off at the bottom of the tower.

It was calculated that under optimum conditions the reaction time would be 1.5 hours, at 180°, using a 7-stage reactor and 10 moles of benzene per mole of sulfuric acid. The same process operated batchwise at 160° to 180° C. required 14 hours and 6 to 8 moles of benzene per mole reacted, and the product contained 1.0 to 1.2% of diphenyl sulfone. Thus, the continuous method increased by nearly ten times the capacity of the batch method. It was further estimated that the ratio of benzene required to benzene reacted could be reduced as low as 3 to 1 by doubling the time of reaction.

Prior to World War II, the I. G. Farbenindustrie, Hoechst, investigated the manufacture of 2-naphthalenesulfonic acid from naphthalene and sulfuric acid by a continuous process, as it was conceived that the large volume of reactants consumed daily—i.e., 33,000 pounds each—would be in favor of continuous processing.

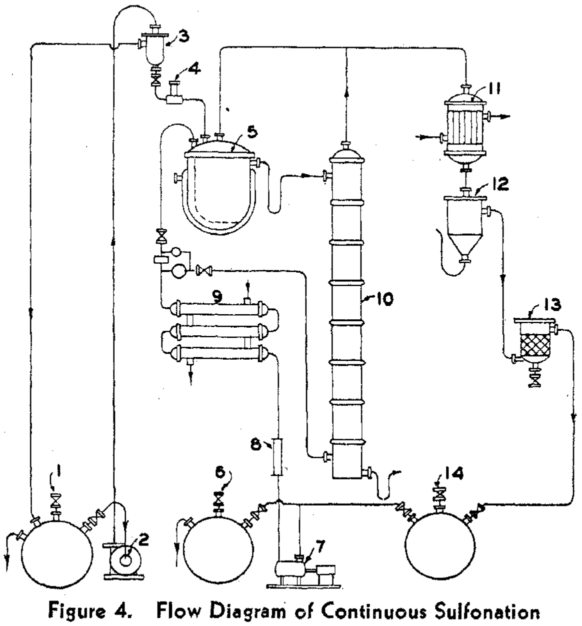


Figure 4. Flow Diagram of Continuous Sulfonation

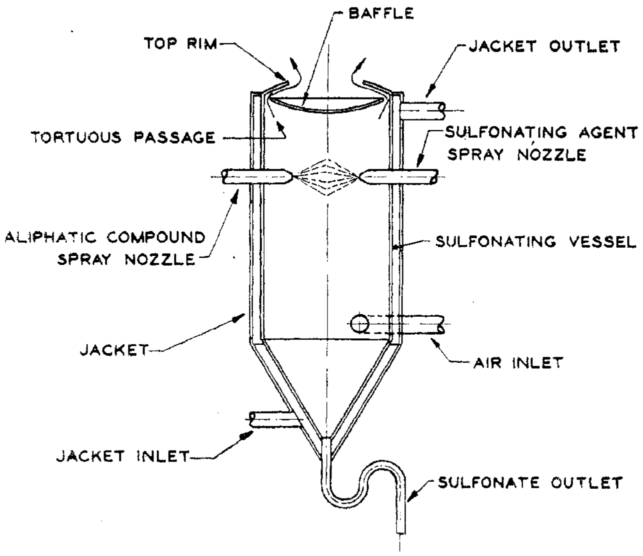


Figure 5. Continuous Sulfonator *(236)*

> In this process, naphthalene and 96% sulfuric acid were premixed at 135° C., and the mixture was passed continuously into a sulfonator maintained at 163° C., from which the sulfonation mass overflowed to a hydrolyzer, in which the 1-naphthalenesulfonic acid by-product was decomposed at 150° with steam, and from which the residual 2-naphthalenesulfonic acid was conducted to a stock tank for subsequent processing.

Although the batch process yield of 84 to 85% was equaled, it was concluded that a further study of agitation was desirable before a final decision was reached as to the merits of the process *(170)*.

Brandt *(47)* patented a continuous process for manufacturing organic sulfonate products of unusual purity.

> The process comprises dissolving a sulfonating agent, such as oleum, and a mixture of aromatic and unsaturated aliphatic hydrocarbons in separate portions of liquid sulfur dioxide, continuously flowing said solutions into a mixing and reaction zone at a low subatmospheric sulfonation temperature (−20° to + 5° C.), thereafter diluting the reaction mass with water to stop undesirable chemical reaction, evaporating the sulfur dioxide from the reaction mass, and finally separating the sulfonate products therefrom, as by neutralization and spray drying.

In the field of aliphatic compounds the I. G. Farbenindustrie, Hoechst, during World War II manufactured large quantities of sulfonate products by the Reed reaction, wherein Mepasin (a hydrogenated Fischer-Tropsch fraction boiling from 220° to 320° C. and containing an average chain length of 15 to 16 carbon atoms) was treated with sulfur dioxide and chlorine in the presence of actinic light in a continuous manner, and the resulting sulfonyl chloride was hydrolyzed to the sulfonate.

> The process was started by charging Mepasin into a 2 × 7 foot reactor illuminated with ultraviolet light, and then metering sulfur dioxide and chlorine into the reactor through a simple ring distributor, during which the contents were circulated through a cooler to maintain a temperature of 25° to 30° C. When the concentration of the sulfonyl chlorides reached 45 to 50%, continuous controlled withdrawal of a portion of the reaction mass was started, while the introduction of fresh reactants was adjusted to maintain the concentration of sulfonyl chlorides. The reaction product was treated with aqueous caustic soda to form the sulfonates, and the unreacted Mepasin was recovered and recycled *(26, 31)*.

The I. G. Farbenindustrie discovered a superior process for sulfonating saturated aliphatic hydrocarbons, which employs sulfur dioxide and oxygen in the presence of actinic light or an acid chloride, acid anhydride, or ketone as a catalyst. This so-called "sulfo-oxidation" process, which also may be operated continuously, yields virtually the same sulfonate products as are obtained by the Reed process, and is said to offer advantages in yield, elimination of the hydrolysis step, power savings, and simplification of plant construction and maintenance.

When the sulfoxidation process is effected with the preferred catalyst acetic anhydride, it must be performed in two stages: In the first the hydrocarbons containing 2.5% added acetic anhydride are gassed with sulfur dioxide and oxygen to convert them to so-called per compounds, which in the second stage are converted to sulfonic acids by treatment with further sulfur dioxide and oxygen in the presence of additional initial hydrocarbons and water; the latter effect a separation of the sulfonic acids from sulfuric acid formed in a side reaction, and from acetic acid formed from the acetic anhydride. The process using actinic light may be performed in a single-stage operation in the presence of water, but it is said to be less attractive, owing to the high power and lamp maintenance requirements. Table III compares the material requirements of the Reed and preferred sulfoxidation process applied to the formation of sulfonates from Mepasin *(26, 31)*.

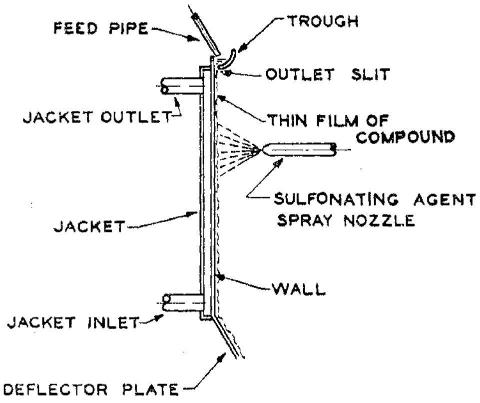


Figure 6. Continuous Sulfonator *(237)*

Partisch and Fraser & Fraser Ltd. *(236)* disclose a novel method for sulfonating aliphatic compounds, such as fats, fatty alcohols, and unsaturated fatty oils, which may be performed in the apparatus shown in Figure 5.

> The aliphatic compound and sulfonating agent are introduced separately into a jacketed reaction chamber in finely divided condition through spray nozzles mounted diametrically opposite each other. At the same time cooling air is blown into the chamber through a tangential inlet and spirals upward through the reaction zone. In this manner the jets of reagents meet and commingle in the presence of swirling cooling air, which leaves through a tortuous annular passage between a deflector plate and a baffle at the top of the chamber, while the particles of sulfonic acid gravitate and leave the chamber through a bottom outlet.

Table III. Materials Consumption

[Kg. per 1080 kg. of sulfonate (= 1000 kg. of sulfonic acid)]

	Sulf-oxidation	Sulfo-chlorination
Mepasin	746.8	796
Sulfur dioxide	422.8	281.6
Oxygen	105.6	...
Chlorine	...	312.4
Acetic anhydride	90	...
Sodium hydroxide	246.6	351.8
By-products and recoveries		
Hydrochloric acid	...	161
Sulfuric acid	270[a]	...
Acetic acid (as acetic anhydride)	68	...

[a] 75% is recovered in usable form.

The process is allegedly advantageous in that it provides products of high quality, permits excellent temperature control as well as a rapid reaction, and avoids the necessity for using excess sulfonating agent. These inventors (*237*) disclose another continuous method and apparatus for sulfonating aliphatic compounds of the foregoing type as well as aromatic compounds—e.g., aniline. A suitable apparatus is illustrated in Figure 6.

The compound to be sulfonated is delivered through a charging pipe to a trough disposed at the top of a jacketed wall, and discharges therefrom through a slit as a thin film of liquid, which flows down the exposed surface of the wall. At the same time a sulfonating agent is sprayed through a nozzle into the descending film of liquid, and the sulfonic acid produced passes downward and is guided to a receiver by a deflector plate at the lower edge of the wall. In this manner, the reactants are intimately mixed in ambient and freely movable air, which affords an ample cooling reservoir assisted by heat exchange through the medium circulated in the jacket so that the temperature of the reaction zone is kept practically constant. The process affords advantages similar to those described in the preceding process (*236*).

A patent assigned to the Colgate-Palmolive-Peet Company (*221*) discloses a continuous sulfonation apparatus for preparing detergents, etc., illustrated in Figure 7. An outstanding feature of this apparatus is that it provides exceedingly vigorous agitation and intimate mixing of reactants coupled with good control of reaction temperature.

The apparatus comprises a vertical cylindrical shell having a central agitator shaft carrying a series of radial mixing paddles, which are arranged to rotate within spaces between horizontal annular cooling members positioned within the cylinder. The four upper cooling members are somewhat smaller in diameter than the inside of the shell, and are connected at their outer edges by cylindrical rings, so that a portion of the liquid in the mixture may flow upwardly from below the fourth member between the wall of the mixer and the peripheries of these upper annular members, and thus be mixed thoroughly with fresh liquid as it enters the mixer. This action is aided by the construction of the paddles in the upper part of the sulfonator.

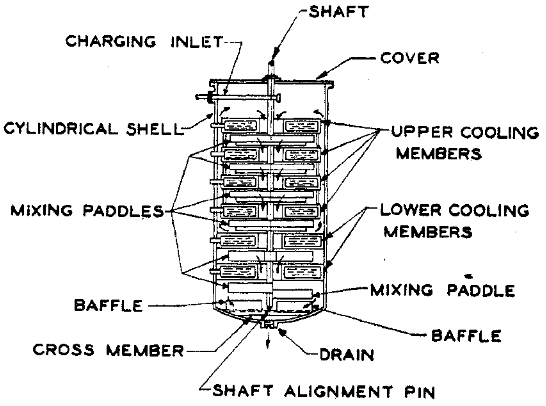


Figure 7. Continuous Sulfonator *(221)*

Each of the three upper paddles consists of a flat circular plate with four vanes extending helically above it to throw the liquid outwardly, and four helical vanes below the plate to draw the liquid inwardly and propel it downward through the center opening in the underlying cooling member. The flat circular portions of the paddles prevent any of the liquid from passing down along the shaft, thus forcing it to travel around the edges of the upper paddles. The fourth paddle from the top is an impeller similar to the upper three, but its upper and lower vanes are arranged to throw the liquid outwardly, and thus force a part of the liquid to return to the top of the mixer. The two lower cooling members fit snugly to the shell so that the liquid must pass through the central openings therein surrounding the agitator shaft. The lower paddles are double radially projecting arms fastened to the shaft. To prevent rotation of the liquid in the mixer and to direct the liquid through the drain opening a pair of baffles is provided at the bottom of the sulfonator.

In operation, the reactants are introduced continuously through separate charging pipes at the top of the sulfonator and pass downwardly while being vigorously mixed and reacted, and cooled by circulation of cooling water through the hollow heat exchange members, and the reaction mass, completely reacted, flows out through the bottom outlet, for subsequent neutralizing and drying.

Berl (*24*) patented an improved contact apparatus of the packed tower type for conducting continuous operations between liquids or liquids and gases, which is said to be particularly suited for effecting nitration and sulfonation reactions. The improvement provides a series of baffles, which deflect the ascending and/or descending liquids or gases from the wall of the tower toward its middle so as to prevent channeling along the wall and to provide a more even distribution of fluid throughout the cross section of the tower.

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