Sulfation and Sulfonation. Practical Aspects

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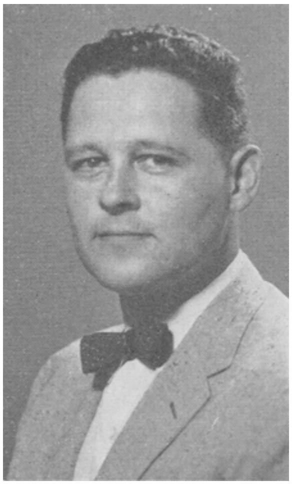
Sulfation is the process of adding the SO_3 grouping to an organic molecule in such a way that sulfur is linked to the carbon through an oxygen bridge. This may be accomplished through direct addition of sulfur trioxide to an alcohol, addition of sulfuric acid to the double bond of an alkene, or by the reaction of a complexed sulfur trioxide with an alcohol. If an alcohol is not used as the organic starting material, the elements of water must be present in the reaction medium. The carbon-oxygen-sulfur linkage is the common property of all organic sulfates. Sulfonates differ from sulfates in that no oxygen bridge is involved, sulfur being bonded directly to carbon. This basic difference in structure between the sulfates and sulfonates is responsible for the differences in chemical properties, notably stability to hydrolytic action in an acid medium, which dictates differences in processing techniques.



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Practical aspects imply the how to and why of performing these unit processes in standard industrial practice. The how to is naturally the culmination of considerable technical effort on the part of many chemists and engineers engaged in research and development in the surface-active field. The why is largely wrapped up in economics, which also influences the direction in which research and development are channelled and therefore has exerted a strong effect on current techniques.

Commercially the most important sulfates are the so-called lauryl sulfates based on straight-chain alcohols derived from coconut oil and closely related longer-chain alkyl sulfates based on tallow. These are hydrogenated and converted to the corresponding saturated straight-chain alcohols by either sodium reduction or high-pressure catalytic hydrogenation. The alcohols are then sulfated and neutralized to form the desired alkyl sulfates. The most important sulfonates are those derived from benzene, now a petroleum product, alkylated with a petroleum-derived propylene tetramer, and sulfonated. Chemically each of these compounds is representative of the other members of its series. However rather wide variations in physical properties may be attributed to variations in chain length, position of the functional grouping, and variations in the configuration of the organic portion of the molecule. Frequently the physical differences in melting point, water solubility, foaming properties, and viscosity-temperature characteristics necessitate adaptation of processing methods. Therefore both chemical and physical properties of the reactants and products of the reaction must be considered in the design and operation of processing equipment used in technical sulfations and sulfonations (2).

Choice of Sulfation Process

Sulfating Agents. In considering which of a number of available sulfating agents to employ in a technical sulfation, it is first necessary to ascertain the desired characteristics of the finished product. At present the alkyl sulfates are quite variable in composition, depending upon the end-product application. The variations include high completeness reaction products for application in the drug field, products formulated to contain about 10% of the alcohol content as free alcohol for use where the optimum in foam volume and stability are required, low salt-content for use in formulating liquid products of relatively high activity and low viscosity and cloud point, and high salt-content where added electrolyte serves to increase the detergency of the final formulation. Choice of either batch or continuous processing is based on volume and continuity of production.

Disregarding these factors, there are three readily available types of sulfating agents. These are chlorosulfonic acid, sulfuric acid, and the various strengths of oleum and sulfur trioxide or Sulfan. In particular, chlorosulfonic acid and sulfur trioxide are well suited to batch processing in that they may be used to produce products of relatively low salt-content and high completeness. Where high salt-content is not objectionable or even desired, and where volume warrants, continuous processing with oleum or sulfuric acid may be indicated.

Batch Sulfation. Assuming that a batch process seems to be the more desirable, it is necessary to choose the sulfation process which is at once the most economical and most compatible with existing plant operations. Consideration must be given to the life of equipment, external dangers to other portions of the plant through corrosion, waste disposal, and air pollution from noxious vapors, and the available personnel. In general, the choice is between using either chlorosulfonic acid or sulfur trioxide.

Of the two, sulfur trioxide offers the advantage of economy; only 80 lbs. are required per mol of alcohol sulfated as compared with 117.5 lbs. of chlorosulfonic acid. In addition, the per-pound cost of sulfur trioxide is less than that of chlorosulfonic acid. On the other hand, if sulfur trioxide is used as the sulfonating agent, a properly designed dilution system is required to ameliorate the intensity of the reaction so that local overheating and side reactions can be held to a minimum. Color and odor requirements of alkyl sulfates today are such as to require extreme care in their manufacture. At times, even with the best designed dilution system, the finished product will require bleaching to meet color specifications. This is also true in the use of chlorosulfonic acid, but the intensity of this reaction is somewhat less than that of the sulfur trioxide one.

An additional plus for the sulfur trioxide reaction is that a virtually salt-free product can be obtained simply by the rigorous exclusion of all water from the reaction mass. In fact, where it is desired to produce an entirely chloride-free product, sulfur trioxide sulfation followed by neutralization with a chloride-free base is the only feasible route.

Advantages of the chlorosulfonic acid method are that trace amounts of water in the reacting mass are not nearly so critical in their effect on the characteristics of the finished product. To the extent that water reacts directly with the sulfating agent, in sulfur trioxide sulfation, the sulfuric acid remains in the reaction mass. This in turn displaces the reaction equilibrium in the direction of forming an alkyl sulfuric acid-sulfuric acid mixture in which the completeness of reaction is low and the resultant neutralized alkyl sulfate is excessively high in both free fatty alcohol and inorganic sulfate. Excess of either can be the cause of excessively high viscosity and will result in poor control of the actual chemical composition and performance of the finished product. Small amounts of water in the chlorosulfonic acid process however result primarily in the requiring of an excessive amount of sulfating agent. Water present in the reaction mass is largely stripped out by the HCl gas evolved during sulfation and in the final stripping operation.

Refrigeration obtained from the evolution of HCl is of value in preventing local overheating, but the necessity for disposing of HCl is probably the most serious drawback. Special ducting systems are required, and although the HCl may be absorbed and utilized as hydrochloric acid elsewhere in the plant, standard practice is to treat it as a waste material. An alternative method not widely used is to recycle the HCl through suitable absorption equipment, reacting it with additional sulfur trioxide to form fresh chlorosulfonic acid (2).

In the case of sulfur trioxide, specialized handling equipment to eliminate fuming is necessary. The fumes themselves are not hazardous, but the dense fog resulting from a small amount of sulfur trioxide released in moist air can be quite troublesome. Precautions must be taken to insure adequate venting of equipment and pipelines, and desiccant protection of the storage tank is essential.

Continuous Sulfation

The other possible choice of process is that of continuous rather than batch operation. In this case oleum or sulfuric acid is the indicated sulfating agent. Such a process does not offer the flexibility of product formulation afforded by either of the two batch processes just mentioned. However it is the more economical method of producing large tonnages of alkyl sulfates where the desired end-product contains a considerable proportion of inorganic sulfate as builder or diluent. The system has been most successfully employed for the production of alkyl sulfate slurries intended for subsequent spray drying to a 30 to 40% active powder employed as a light-duty household detergent. The major problems involve the selection of the proper strength and ratio of the sulfating agent, sufficient heat-exchange capacity to remove the heat of reaction at a reasonable temperature, and consideration of the system volume, which in turn governs the reaction time and the yield of the desired product.

In any system employing sulfuric acid or any of the lower strength oleums, hydrolytic stability of the alkyl sulfuric acid in the presence of sulfuric acid is a major consideration. Thus it is good practice to use a large excess of the sulfating agent to effect rapid sulfation, thereby reducing the formation of dialkyl sulfate, and to take up the water of reaction. It is then necessary to neutralize the reaction products just at the point of maximum formation of alkyl sulfuric acid. Delay results in a reduced yield of the monoalkyl sulfate.

Excessive reaction time favors the formation of an increased amount of dialkyl sulfate, which in turn is hydrolyzed in the neutralization step to the monoalkyl sulfate and free alcohol. Furthermore oversulfating leads to such side reaction products as ethers and alkenes.

Depending upon the operating temperature and the quantity and strength of the sulfating agent employed, reaction time is in the range of from 10 seconds to three to four minutes. If, for a given set of conditions, an optimum reaction time of two minutes has been determined, it will be found that a variation of from 10 to 15 seconds in the reaction time (obtained by altering system volume or through-put) will result in a reduction of from 10% to 15% in the formation of the desired alkyl sulfuric acid. Excessive reaction time promotes formation of dialkyl sulfates, insufficient time prevents adequate sulfation, and the result of either of these departures is excessive free-alcohol in the neutralized product. Oversulfation is the more serious in that incomplete hydrolysis of the dialkyl sulfate in the neutralization step results in pH drift of the final product at or near the neutral point. This characteristic generally requires buffering of the neutral product or neutralization of the product to an alkaline pH between 9.5 and 10.2.

Over- and undersulfation obviously are to be avoided, and, notwithstanding the rather rigid controls required, continuous sulfation for the production of medium active alkyl sulfates is economically attractive. Major advantages of this method over batch methods are product uniformity, over-all product economy, small space requirements for large capacity, and reduced product storage requirements. Considerable research and development work is being carried on to overcome the obstacles to continuous processing using sulfur trioxide. Most of this work involves the use of recoverable gas diluents, such as sulfur dioxide, which also remove the heat of reaction. So far no successful process of this type has been commercially announced.

Operating Conditions

Temperature. In the operation of either batch or continuous process it is desirable to sulfate at as low a temperature as possible in order to avoid undesirable side reactions. These lead to the formation of color and odor bodies as well as to alkenes, aldehydes, and ethers and seriously impair the usefulness of the end-product. In conventional operation the lower limit of operating temperature is that at which alcohol crystallizes from the reaction mass onto heat-exchange surfaces.

As a practical example, sulfation of lauryl alcohol with sulfur trioxide in a batch system may be considered. The sulfator is designed with proper gas distribution and agitation, and cooling is provided by circulation of the reaction mass through an external shell and tube cooler. Temperature of the cooling water can be varied at will. It is possible to sulfate at a temperature of 100°F. in the sulfator, a normal condition. The temperature in the sulfator is also the temperature of the mass entering the cooler, 100°F.; temperature leaving the cooler will be about 90°F. with cooling water supplied at 80°F. If the temperature of the cooling water is then gradually reduced, circulation is impaired, heat exchange is reduced, and the temperature in the sulfator begins to rise. Increasing the cooling water temperature at this point will reverse this trend, and the original conditions will be restored. This is basically a characteristic of external coolers. The operating temperature can be reduced somewhat by employing cooling within the sulfator itself. The cooling water temperature limitation is the same, but, by cooling the mass continuously, average sulfation temperature can be controlled at close to 5°F. below those obtainable with external cooling (Figure 1).

In sulfating different alcohols and mixtures of alcohols with sulfur trioxide, there is an optimum sulfating temperature for each. In compositions between the lauryl and tallow alcohols, sulfating temperatures range from 100° to 130°F. Use of chlorosulfonic acid will allow some reduction to about 90°F.

Further reduction of the sulfating temperature to about 50°F. or lower is obtainable by employing the liquid phase sulfation with SO_3 dissolved in SO_2 or in an inert hydrocarbon solvent, such as liquid propane or butane. The heat of reaction is taken up by evaporation of sulfur dioxide from the reaction with cooling and condensation in an external refrigeration system. The recovered inert gas is then recycled with additional sulfur trioxide. This method has the sole disadvantage of requiring a high tonnage of mechanical refrigeration. Vacuum stripping of the last traces of the inert diluent is also required if sulfur dioxide is used.

In continuous sulfation of alcohols with sulfuric acid or oleum, temperature is equally important. Because fatty alcohols are to some extent soluble in sulfuric acid and oleum, crystallization of alcohol from the reaction mass occurs at a somewhat lower temperature than when sulfur trioxide is employed. A temperature advantage of up to 15°F., may be obtained in the sulfation of tallow alcohol with 20% oleum as compared with sulfation with sulfur trioxide.

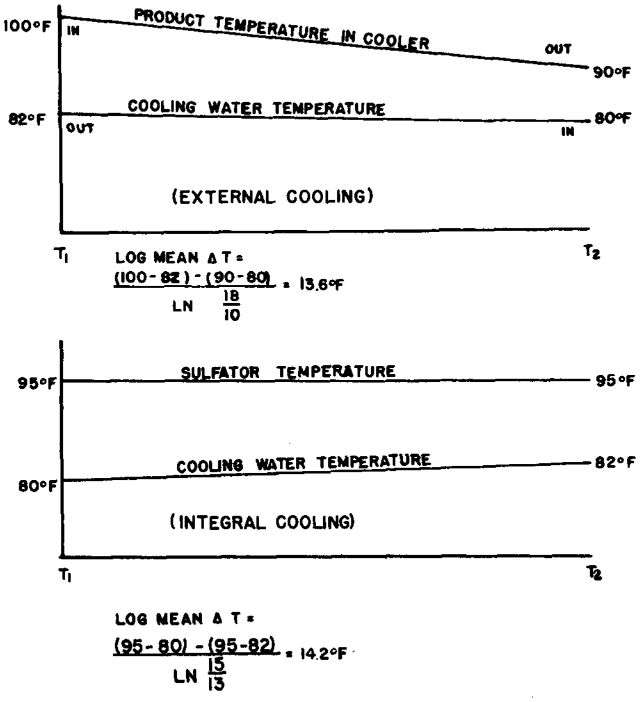

FIG. 1. Temperature gradients for external and integral cooling.

Other Operating Variables

In sulfur trioxide sulfation the important thing is to keep all water out of the reaction. Maintenance of equipment is extremely important. Attention must be paid to water-cooled heat exchangers, water-cooled pump packings, and to the reactants themselves as possible sources of water. In sulfur trioxide sulfation particularly, leakage of as little as five pounds of water into a 2,000-lb. batch of alcohol during the sulfation cycle of two to three hours can result in a completeness reduced as much as 10% below the expected value and in the formation of approximately 100 lbs. of sodium sulfate in the neutralized batch. If low viscosity is desired, such an increase of salt and free lauryl alcohol in the neutralized slurry offsets any advantage gained by employing sulfur trioxide in preference to chlorosulfonic acid.

Similarly water must be rigorously excluded from the alcohol to be sulfated. Careless storage can result in dissolved water in the lauryl alcohol up to its normal saturation level of about 2% at 80° to 85°F. Forty pounds of water in a 2,000-lb. charge of lauryl alcohol gives totally unsatisfactory results. To obviate this condition, alcohol storage tanks should be equipped with desiccant protection in the vent to prevent water pick-up during the normal breathing of the tank during filling and emptying. Provisions are made for periodic regeneration of the desiccant bed.

Storage of Sulfan and chlorosulfonic acid both require moisture absorption systems to prevent obvious difficulties. In the case of Sulfan, trace amounts of moisture result in the destruction of the boron oxide stabilizer and subsequent polymerization of SO_3 to $(SO_3)_x$. In the case of chlorosulfonic acid, moisture results in hydrolysis of the acid to sulfuric acid and wet HCl vapor, which is corrosive to equipment. Handling and storage facilities for Sulfan are described in bulletins issued by the General Chemical Division (1).

Neutralization

The technique of neutralization is also quite important. To neutralize a hydrolytically unstable product in aqueous medium, it is essential that conditions be controlled so as to keep hydrolysis to a minimum during the neutralization period. Three principles are applied at this point. Temperature of the neutralizing medium is maintained at or slightly above the freezing point of the alkyl sulfuric acid feed. This prevents formation of gel-like lumps of congealed alkyl sulfuric acid which include moisture in their structure and tend to hydrolyze. The pH of the bath is maintained above the equivalence point.

Adequate agitation is provided to insure uniformity and to break up any agglomerates which tend to form. Turbine agitators in batch processing or centrifugal in line mixers in continuous processing are good practice. Further, particulation of the acid stream entering the neutralizer is an aid to more efficient mixing.

Neutralization to final pH is generally followed by buffering in all but amine-neutralized systems which are self-buffering above a pH of 7.

Product Handling and Storage

In general, pumps, piping, and tankage for handling finished alkyl sulfates are fabricated from 300 series stainless steel. The choice between 304 and 316 is largely one of individual preference. Where pumps are concerned, it is often more economical to specify higher alloy materials because these pumps are stock items whereas the 304 and 316 alloys are obtained on special order. Tanks or piping of aluminum alloys, monel and glass, or plastic-lined steel tanks are generally satisfactory for alkali-neutralized products. One exception is that monel or other copper-bearing alloys are unsatisfactory for amine and ammonium compounds. Certain copper-bearing aluminum alloys are also harmful. Often in high concentration slurries, heating is necessary to maintain fluidity for pumping. Heating coils are generally provided in storage tanks. The heating medium is advisably hot water rather than steam to prevent any tendency to hydrolysis. Using a water temperature of 150°F. and maintaining a product temperature of 130°F. for as long as four months results in no detectable hydrolysis. To illustrate further the effect of heat on the stability of the alkyl sulfates, a test was conducted with a 35% active sodium tallow alcohol sulfate slurry (Table I). Samples were sealed in glass ampoules and heated to various temperatures, to which the product might be subjected in drying or further processing.

Depending upon the steam pressures, steam coil heating may be safe. However failure of a regulating valve or local overheating at the heating surface because of poor circulation may cause hydrolysis to start at that point. Hydrolysis is autocatalytic in that the acid thus formed hastens further hydrolysis. In a large mass of material, heat of hydrolysis raises temperature rapidly and subsequent reaction proceeds quite violently.

Recovery of Alcohol

If for some reason it is desired to recover fatty alcohol from an alkyl sulfate, acid hydrolysis in suitable equipment is a satisfactory method. The resulting alcohol need only be distilled for re-use in processing. To initiate the hydrolysis, only heat is required. However, to dispense with a rather long induction period at atmospheric conditions, sufficient acid is added to bring the pH below about 3.0 before boiling. To get a complete split and good phase separation, acid concentration in the water phase should be reduced to below 5% as H_2SO_4 in the final boil.

Sulfonation

Process Selection. In alkyl benzene sulfonation, the choice lies between batch and continuous processing. The principles of choice are the same as in sulfation. Large volume of a particular sulfonate indicates continuous processing while batch processing is well suited to small or irregular production demand and to the manufacture of a variety of sulfonates. For continuous sulfonation, continuous dilution and separation of the spent sulfonation acid may be employed. Continuous neutralization is optional, depending upon whether the sulfonic acid or the neutral sulfonate is the desired product. Again as in the case of sulfation, process variables are controlled to give the maximum yield. High completeness products of good quality may be produced by exhaustive sulfonation under controlled conditions or by solvent extraction of unsulfonated oil from incompletely sulfonated material. The choice of sulfonating agent is generally limited to two, sulfuric acid or oleum up to about 30% SO_3 in the liquid phase, or Sulfan or sulfur trioxide in the vapor phase. Chlorosulfonic acid may be used, but the reaction is more complex and the reagent more expensive than those in general use. In addition, the fact that the sulfonic acids are stable to hydrolytic action makes possible production of high activity material even with the weaker sulfonating agents merely by separation of spent acid.

TABLE I

Time-Temperature Stability of Sodium Tallow Alcohol Sulfate—35% Active Aqueous Slurry pH 8.5

Sample No.	Temperature, °F.	Time exposed, min.	Hydrolysis, %
1	212	10	0
2	240	10	Tr
3	265	10	31
4	280	10	100[a]

[a] Complete separation into two phases within 5 min. at 280°F.

Batch Sulfonation. Equipment used for sulfation of alcohols with sulfur trioxide can be used interchangeably for production of alkyl benzene sulfonates. Sulfonation is carried out by introducing SO_3 diluted to 10% to 15% concentration with air or other inert gas into a stirred and cooled mass of alkyl benzene. If the temperature is controlled to about 90°F., approximately 0.34 lbs. of SO_3 per lb. of alkane introduced over a period of two hours is required to yield a sulfonated product of about 96% completeness with 3% oil content on the dry salt-free basis. Normally the sulfonation is complete at the end of the SO_3 addition. However, if higher completeness is required, a subsequent digestion period of from one to two hours at the sulfonation temperature is sufficient to reduce oil content to about 1.5%.

Similarly 98% sulfuric acid may be used as the sulfonating agent, but in a liquid phase reaction. Approximately three times the weight of alkane of the 98% acid should be added over a period of one to two hours. Temperature is maintained at about 90°F. with a one- to two-hour digestion period following sulfonation. The product is diluted from its approximately 90% acid strength to 80% with water, and the spent acid is separated. The characteristics of color and completeness of this product are similar to those obtained by a lesser quantity of sulfur trioxide. The apparently large excess of acid required is caused by the fact that the reaction stops altogether when residual acid strength falls to 90%. This pi value (3) has been determined for a number of aromatic compounds and varies with differences in the aromatic nucleus and with the structure and number of substituents.

Where oleum strengths between 10% and 30% are used, the amount of sulfonating agent required is greatly reduced. This is true because as long as the acid strength is above 100% sulfuric acid, the reaction can be assumed to proceed by direct addition of SO_3 to the organic nucleus. Below 100% acid strength one mole of water is formed for each mol of sulfonic acid, and this seriously reduces the effectiveness of the acid. As has been previously pointed out in published reports (4), higher strengths of oleum above

30% are not practical on account of the high melting point and the undesirable side reaction products formed by concentration of the reagent in liquid-phase systems.

An additional method of sulfonation recently introduced makes use of an SO_3–SO_2 system, which is uniquely suited to the manufacture of high-quality sulfonic acid (5). The increased cost of operation is largely offset by the fact that the sulfonic acid so produced is stable as to color and odor for protracted periods of storage. This can be stored and shipped readily to individual formulators, who in turn can neutralize and blend it to form a number of products. The advantage of shipping only about 40% of the weight required for shipping equivalent active in the form of so-called concentrates is obvious. The low sulfuric acid content of the now commercially available sulfonic acid makes it adaptable to formulation of the popular liquid detergents by smaller producers.

Continuous Sulfonation

If continuous sulfonation is indicated for production reasons, any of a number of package plant installations are available. A number of variations in method are used, each differing from the other in certain engineering features auxiliary to the basic process. One variation involves apportioning the sulfonating agent to each of several sulfonating stages, thereby distributing the reaction heat load over several reactor systems. Another feature is that of employing shorter through-put time at the expense of increasing the quantity of sulfonating agent. The advantage rests in the reduction of the size of the installation for a given production rate and better response to the control of process variables. Spent acid may be separated by continuous centrifugation in one system or by gravity in specially designed separators in another. All these engineering refinements are designed to produce the desired product in the shortest possible time consistent with finished-product quality and economy. Systems have been designed where the through-put time from raw material to finished neutralized product is as short as 30 min.

Sulfonation itself can be accomplished with excellent yield and quality in as little as five minutes through-put time. Optimum operating temperature from the standpoint of completeness alone is approximately 160°F. with the modern high quality alkanes. However color and odor considerations usually dictate an operating temperature below 140°F. The major deterrent to higher temperatures of operation is usually inadequate mixing.

Three types of continuous reactors are available for continuous sulfonation. These are the homogeneous or dominant bath type, the staged reactor, and the heterogeneous type. In the dominant bath type of reactor (6) fresh reactants are introduced and mixed continuously into a medium composed of previously reacted material. This mass is continuously circulated through a heat exchanger to remove the heat of reaction and is allowed to overflow into a digestion chamber continuously. The ratio of reacted material recirculated to fresh reactants is maintained rather high so that the composition of the material at any place within the reactor is substantially the same. Consequently the reaction medium is homogeneous. The overflow from the digestion stage in this system is then either separated from its spent acid or neutralized directly to form an alkyl benzene sulfonate slurry. The staged reactor makes use of the same principle except that the sulfonation is conducted in several (up to five) discrete steps. Each step operates on the overflow from previous steps and is reported to yield a product of higher quality than that obtainable from the older one-step system. The heterogeneous reactor relies on the fact that when fresh alkane and sulfuric acid are mixed continuously in the bottom of a vertical tank sulfonator, the reactants are progressively displaced upward and are allowed to overflow from the reactor and either separated from the spent sulfonation acid or neutralized directly into an alkyl aryl sulfonate slurry. Sulfonation and digestion take place simultaneously throughout the reactor, and material at various levels is variable in composition. Integral cooling is provided, and the reactor is generally provided with baffling to prevent back-mixing. The dominant bath and heterogeneous reactors are illustrated in Figures 2 and 3 along with a list of typical operating conditions.

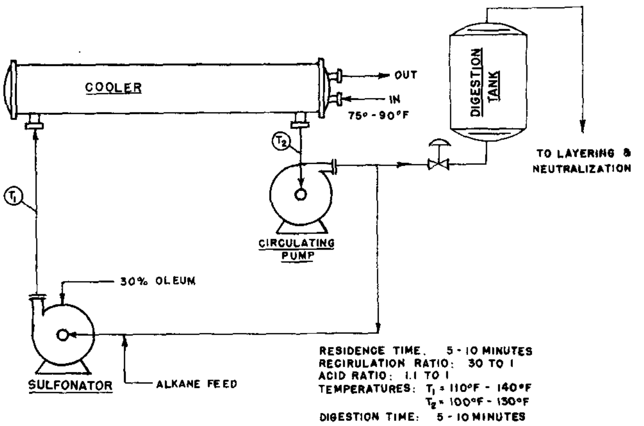

FIG. 2. Homogeneous continuous sulfonator.

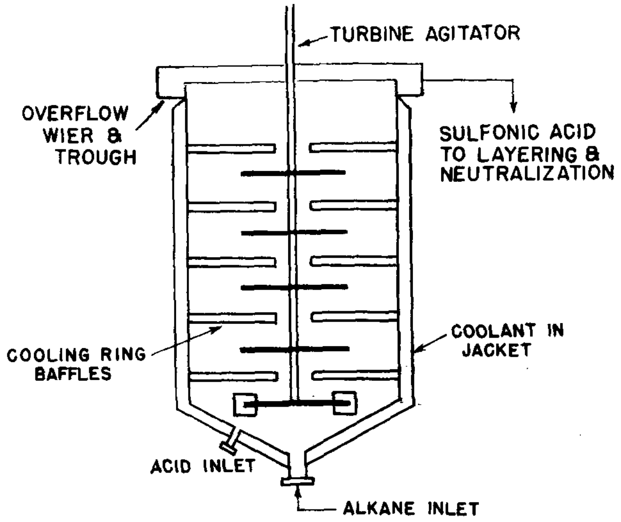

FIG. 3. Heterogeneous continuous sulfonator.

The capacity of such systems is limited only by the choice of components and the operating conditions selected. In general, a heat exchange area of one square foot for each five to 10 lbs. of hourly capacity of alkane is necessary to remove the heat of reaction. Total reaction and digestion time ranges from 10 to

30 min., depending upon the type of system employed. Product is of excellent quality in regard to color and completeness.

Product Storage and Handling

The same general rules apply to the storage and handling of sulfonates as to sulfates, with one notable exception. That is, the sulfonic acid itself can be successfully stored if it is freed of its residual spent acid. Also, since the sulfonates are more stable to hydrolysis, excessive temperature in storage and absence of buffering are not nearly so serious. In materials of construction, requirements are similar except that monel is not advisable in the dilution and layering steps where the acid strength is variable around an average 80%. Finally alkyl benzene, being nonhygroscopic in nature, requires none of the special protection necessary for the handling and storage of lauryl alcohol.

Summary

There are a number of approaches to the problems involved in technical sulfations and sulfonations. These involve the choice of either batch or continuous processing, depending upon consideration of the projected volume, the variety of products to be manufactured, and the ultimate disposition of these products. Technical considerations of process design involve selection of process equipment, sizing, piping, and plant layout. For the best results, particular attention must be paid to the control of process variables during actual production. These considerations, together with the application of sound chemical and chemical engineering practices in process formulation, are all essential to the production of high quality organic sulfates and sulfonates for detergent use.

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The Changing Scenes of Syndets and Soaps[1]

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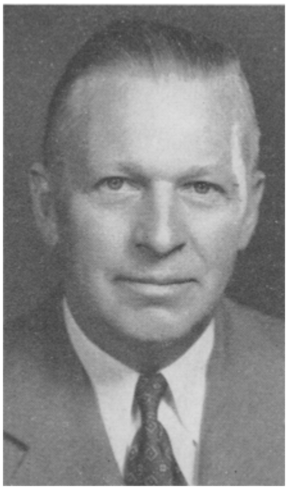
The use of soap, and I'll use this word to include synthetic detergents, is a measure of a country's development. We will take a look at this in two ways, first historically, and second by countries. We'll find that as a country develops, it uses more soap. It would be a great shock in many ways if we were to be subjected to the comic strip, space-time machine and be whisked back to some location around the Mediterranean about 500 B. C. One of our first exclamations would be, "no soap!" Water and oils were both used for cleanliness before soap was available. Cleanliness was, and still is, closely related to religion. John Wesley, founder of Methodism, probably made the most famous remark about cleanliness when he said about 1750, "cleanliness is indeed next to godliness."



Roy W. Peet

Instructions given in the Koran by Mohammed include the following. "All true believers are strictly enjoined to wash their head, their hands as far as the elbows, and their feet as far as the knees, before saying their prayers; and when water is not to be procured, fine sand is to be used as a substitute." Bathing in the Ganges is believed to wash away sins as well as physical ailments. The development of the relationship between cleanliness and health is not clear, but there was some concept of this in early times. The Egyptians were the chemists of early days, and Egypt was the center of early soap-making. They had precepts or laws involving cleanliness in matters of health, the choice and preparation of foods, and the care of children. The Jewish people likewise had and still have carefully prescribed practices which would seem to be dictated by a sound concept of the relationship between cleanliness and the prevention of disease. Bathing and cleanliness are frequently found definitely associated with periods of deep religious and emotional dedication or action. Where hygiene begins, and where religion or superstition ends, is difficult or impossible to decide.

The rise and fall of the Roman Empire, because of its influence on the political, economic, and cultural world of that day, had much to do with the spread of running water, sanitation, and cleanliness. The Roman aqueducts carrying water to the cities from far-away sources are marvels of conception and execution. Water made possible the big public baths that still remain as tourist sights. The Romans took to bathing in a big way and had hot water, steam rooms, and cold plunges. Prior to the time of soaps they used a kind of skin scraper to remove dirt and perspiration in the process of bathing. These baths were not associated with religion but instead were cultural and aesthetic. I understand that the Pennsylvania Station in New York is a reproduction of the Caracalla Thermae in ancient Rome, which provided simultaneous bathing facilities for about 3,000 people.

The Greeks established bathing as an aesthetic pleasure and practice with no relationship to religion. Marriage was surrounded by a ritual of purification including bathing, but the Greeks valued the bath as a means of creating a feeling of well being, to enhance the beauty of the individual through cleanliness, and to suppress unpleasant body odors. There

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[1] Dinner lecture.