SESSION IV
Processing and Packaging

Sulfonation and Sulfation Technology

A. LANTERI, G. Mazzoni S.p.A., P.O. Box 421, 21052 Busto Arsizio, Italy

ABSTRACT

The paper will summarize the sulfonation/sulfation process used in the detergent industry, with particular emphasis on the modern techniques involving the use of diluted gaseous SO_3 as a sulfonating agent. The outstanding features of the commercially available SO_3-air processes will be described, and the Ballestra, Berol, Allied, Chemithon, and Mazzoni reactors will be shown graphically in figures. The particular aspects of processing the various feedstocks, decomposition of the by-product anhydrides in sulfonation of alkylbenzene, hydrolysis of the sultones formed in sulfonation of alpha olefins, and their implication on the integrated sulfonation processes are also considered.

INTRODUCTION

The purpose of this paper is to present a general survey of new sulfonation and sulfation techniques. Sulfonated and sulfated products constitute the major part of the world production of surface active substances. With a few exceptions, such as secondary alkane sulfonates obtained directly from n-paraffins by reaction with SO_2 and O_2, the most important materials of this group are made by sulfonation or sulfation of organic raw materials such as alkylbenzenes, fatty alcohols and their low mole ethoxylates, and alpha olefins.

Sulfur trioxide, oleum, sulfuric acid, and chlorosulfonic acid are the usual sulfonating/sulfating agents. At present, oleum and sulfuric acid are mainly used for sulfonating alkylbenzenes. Due to the excess of acid required in sulfonating, the neutralized product contains considerable sodium sulfate. The addition of more water after sulfonation causes a separation of most residual acid, but this procedure gives rise to a spent acid disposal problem. Chlorosulfonic acid is used for sulfating fatty alcohols and their ethoxylates. The reaction is stoichiometric. However, the hydrogen chloride which evolves during the reaction must be absorbed in water and this again creates an acid disposal problem.

Sulfur trioxide reacts with most organics on a mole to mole basis. Usually only a moderate excess of SO_3 is required to sulfonate or sulfate them almost quantitatively. Increasing demand for highly active products has centered attention on SO_3 sulfonation/sulfation. In addition to the more traditional active ingredients, such as alkylbenzene sulfonates and alcohol sulfates, potentially important surfactants such as alpha olefin sulfonates and fatty acid ester sulfonates may be efficiently produced via SO_3 routes.

Three product quality factors must be considered in the production of detergent sulfonates or sulfates: light color, low free oil, and low inorganic salt. The problem of product color is very important for economic and commercial reasons. For many applications, a color of 60 Klett or less (on 5% active solution) is required. Attempts to cope with the extreme reactivity of SO_3 and the high heat of reaction have led to many different process designs.

One of the oldest commercial systems utilizes liquid SO_2 as evaporating solvent (1,2). This procedure offers the advantage of very low reaction temperatures for control of the product quality. However, the use of SO_2 makes the procedure quite laborious.

A process developed by The Andrew Jergens Co. (3,4) uses SO_3 vapor under reduced pressure by contacting with the organic reactant in a mixing nozzle. The process uses the "dominant bath" principle, i.e., recirculating the organic material through a heat exchanger and then back to the mixing stage, for quickly absorbing the heat of reaction.

For practical reasons, the most widely used method of moderating the reaction of SO_3 is to employ it as a vapor diluted with inert gas. Commonly a clean dry air-SO_3 mixture is used, which may be produced by any of the following three ways:

1. vaporization of stabilized liquid SO_3 in an air current,
2. stripping of high strength oleum and vaporization of the distilled SO_3 as above,
3. burning of elemental sulfur and subsequent catalytic conversion of SO_2 to SO_3.

All these systems require a supply of dry air in an amount and at a pressure dependent on the particular sulfonation process.

An attempt is made here to present the outstanding features of the air-SO_3 processes that are known to be in commercial use, particularly those which may be carried out with commercially available equipment. They differ mainly in the ways in which the reactants are contacted, the reaction heat removed, and the reaction product protected from decomposition or discoloration.

BASIC ASPECTS OF SULFONATION AND SULFATION WITH AIR-SO_3

Sulfonation and sulfation with air-SO_3 are fast gas-liquid reactions. The partial pressure of SO_3 in the gas stream determines the driving force for the transport of SO_3 from the gas phase to the liquid and is, therefore, one of the most important process variables. The rate at which the true reaction occurs varies widely with the organic compound. For instance, alpha olefins undergo sulfonation

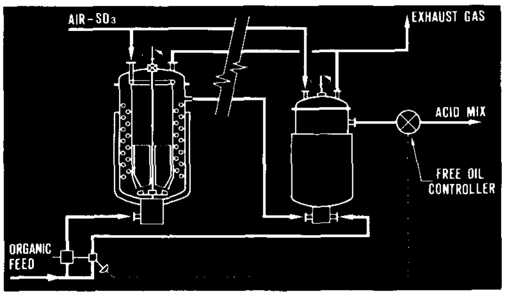

FIG. 1. Ballestra reactor system.

many times as fast as alkylbenzenes with SO_3. It is essential that the concentration of SO_3 in the gas mixture is kept sufficiently low and that the gas is brought in uniform contact with the liquid reactant as quickly as possible. Furthermore, intensive mixing in the liquid phase should be maintained throughout the reaction so that the concentration of reacted molecules at the interface is immediately lowered and other unreacted molecules become available at the interface to react with the gas.

The heat of reaction with SO_3 vapor is about 40 Kcal per mole of SO_3 both in sulfonation and sulfation of most organic compounds in the detergent range. Heat removal must be very rapid in order to maintain the proper reaction temperature according to the viscosity or the freezing point of the liquid phase, and to keep local overheating to a minimum.

The problem of minimizing product degradation is of particular concern when treating certain sensitive organics. In sulfating fatty alcohols, for instance, the acid product tends to undergo dehydration, oxidation, and esterification reactions with formation of alkenes, ethers, aldehydes, fatty acids, and esters. The result is an increase of the petroleum ether extract (apparent unsulfated alcohol) and of the inorganic sulfate content of the neutralized product. As another example, in the sulfonation of alpha olefins, competitive reactions, such as disulfonation and oxidation, tend to subtract SO_3 from the monosulfonation. This may require increasing the excess of SO_3 to obtain a high olefin conversion. However, an excess of SO_3 leads always to a darkening of the product. In general, as the sulfonation of sulfation reaction approaches completion, there is an increased tendency for the acid product to undergo unwanted side reactions.

Another important consideration is air pollution control. In general, the exhaust gas leaving the sulfonation system contains SO_2 (either present in the gas from sulfur burning and/or formed in the sulfonation step as a result of oxidation reactions), some unreacted SO_3, and entrained organic droplets or mist. While SO_2 may be easily scrubbed with alkaline liquors, the removal of SO_3 and organic mist is more difficult and sometimes requires special devices to comply with local environmental regulations. The equipment and operating energy costs for cleaning of exhaust gas will depend on variables inherent to the process and plant operation such as air mass flow rate and concentration of pollutants in the exhaust gas, and the desired removal efficiency.

"DOMINANT BATH" PROCESSES

In a batch process, the air-SO_3 is dispersed into a charge of organic reactant in a vessel stirred by a turbine impeller, and the heat is dissipated according to the "dominant bath" principle. The gas is introduced at a constant rate until the predetermined amount of SO_3 has been reacted with the organic. In the initial stage, it is relatively easy to maintain a good mixing. Moreover, since it is possible to work with a large volume of organic material in relation to the rate of gas addition, the heat of reaction that is developed can be distributed to the cooled surfaces of the apparatus by rapid recirculating in the reaction mixture. However, because the viscosity of the reaction mixture increases steadily with conversion, there is a progressive reduction of mixing intensity and of heat transfer rate.

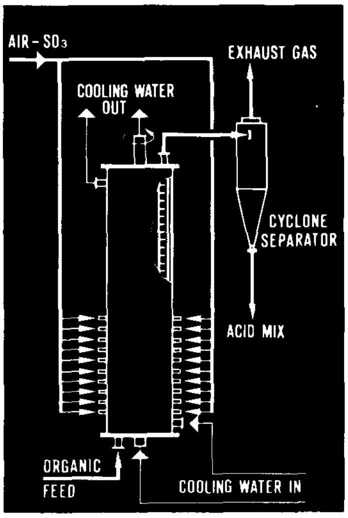

FIG. 2. Berol reactor.

Ballestra

The Ballestra process (4-6) is the first continuous air-SO_3 process which has been introduced on a commercial scale in combination with a sulfur burning system for generating the air-SO_3 mixture.

The sulfonation apparatus (Fig. 1) consists of two or more stirred tank reactors arranged in a cascade sequence. Each reactor is equipped with a special high speed turbine impeller to disperse the gas and circulate the organic reactant. Cooling coils and baffles are positioned within each reactor for efficient heat removal.

The organic feed enters the first reactor, and the liquid mixture overflows by gravity from one reactor to the next. The 7-8% air-SO_3 mixture enters the reactors in parallel and in controlled amounts, with the major portion entering the first reactor and progressively lesser portions entering the subsequent reactors. The exhaust gas leaves each reactor from the top. A small proportion of the fresh organic reactant is fed to the last reactor via a feedback system which controls the free oil content of the sulfonic acid.

Such an arrangement of reactors allows distribution of both gas load and heat load over more reaction stages, with the bulk of the reaction occurring in the relatively low viscosity medium of the first stage and a minor amount in the higher viscosity medium of the last stage. This facilitates heat transfer and the control of temperature in each stage and also reduces the reactor volumes of the last stages. The number and size of the reactors depend on the capacity of the plant. Some units have as many as five or more reactors.

"ONCE THROUGH" PROCESSES

Most of the present air-SO_3 sulfonation/sulfation processes use once-through gas flow along with short residence time reactors. The reactants are generally vigorously mixed either by mechanical agitation or by passing the gaseous reactant at high velocity through the reaction zone. However, a sharp distinction between the commercial systems on the basis of the type of mixing cannot be made. The heat of reaction is simultaneously removed at the reaction sites and/or by immediate cooling of the reaction mixture.

Agitated Zone Processes

Generally, sulfonation/sulfation in agitated gas-liquid

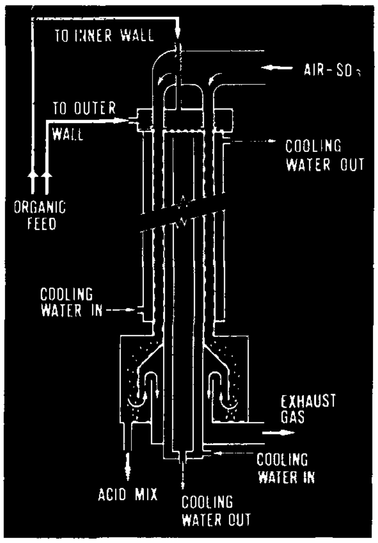

FIG. 3. Allied reactor.

reactors involves stepwise addition of SO_3. This essentially extends the portion of the reactor in which fast reaction takes place leading to a more uniform temperature distribution in the reactor.

In a process developed by Marchon Products, Ltd. (7), the organic reactant flows continuously through a number of mixing stages (up to ten or more), which are separated by interstage coolers. The air-SO_3 is fed in parallel streams to the subsequent mixing stages, except to the last stages, where the completion of the reaction takes place with the SO_3 which is carried over from the previous stages. The exhaust gas is separated from the liquid reaction product after the final mixing stage.

Berol: The reactor of the Berol process (8-10) (Fig. 2) consists of a cooled vertical cylindrical shell and a coaxial inner revolving cooled drum. Only a small annular space is formed between the stationary and the moving cooled surfaces, and this is used as the reaction zone. The surface of the drum carries a large number of small round pins that extend nearly to the shell surface and serve to increase turbulence of the reaction mixture by rotating the drum. The pins are sufficiently spaced to minimize "dead zones" and are arranged in the form of a spiral along the surface of the drum to impart a lateral and advancing movement to the reaction mixture.

The organic feed is introduced through a bottom inlet and the air-SO_3 of about 6% is distributed through two lateral rows of nozzles located in the lower half section of the reactor. Owing to the movement of the rotor, the gas is dispersed throughout the organic reactant as small bubbles, and the mixture is forced upward in the annulus between stator and rotor thus reducing back mixing effects. The reaction mixture is withdrawn at the top of the reactor for gas-liquid separation.

Film Processes

Film sulfonation/sulfation is carried out in gas-liquid cocurrent tubular reactors where the organic moves as a thin film completely circumscribing the wall of the conduit, and the air-SO_3 travels as a turbulent flow at high velocity in the core of the conduit. The heat of reaction is removed by jacket cooling. Most of these devices are single-pass downward flow systems.

Straight cocurrent flow avoids repeated exposure of the liquid mixture to fresh SO_3 as the conversion increases. On the other hand, cocurrent flow causes a sharp rise in temperature in the early reaction stage where the gas stream containing the initial concentration of SO_3 contacts the unreacted organic. Here the rate of mass transfer is high, and the rate of heat transfer is the capacity limiting factor. The temperature reaches a peak value, after which the heat loss to the cooling jacket is greater than the heat of reaction, and the temperature drops. In the last reaction stage, the concentrations of both the gaseous and liquid reactants are small, and the rate of mass transfer becomes the limiting factor. There is some relation between the two factors because an efficient gas scrubbing in the last stage permits reduction of the required excess SO_3, thus also ameliorating the intensity of the reaction in the early stage.

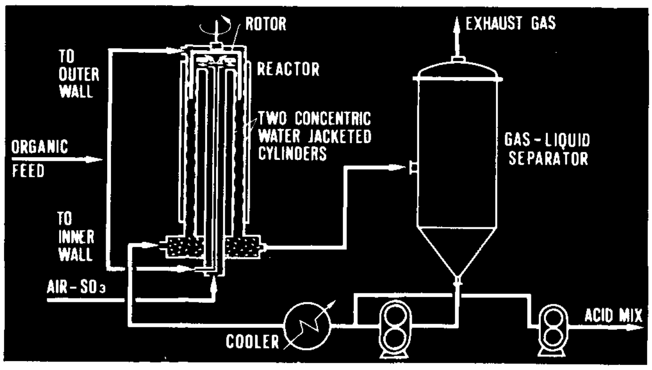

FIG. 4. Chemithon reactor system.

The gas velocity and the hydraulic diameter of the tubular reactor (distance between the cooled reaction surfaces) are the primary design factors affecting equipment performance. Increasing gas velocity will increase the transport rates (film velocity, heat and mass transfer in both gas and liquid phases) and the uniformity of gas-liquid contacting. However, with increasing velocity and turbulence of the gas stream, an increasing amount of liquid is swept from the film surface. The gas velocity in the reactor tube must not be so high as to cause an excessive liquid breakup and carryover of fine droplets by the gas stream. The gas phase transfer rates are sensitive to changes in reactor tube diameter. For a fixed gas velocity, as the tube diameter becomes smaller, a shorter contact length will suffice to obtain an almost complete absorption of SO_3. The smaller diameter tube also permits a more rapid temperature equalization between the continuous liquid stream and the liquid droplets which may be entrained in the gas core. These factors are combined in different ways in the actual units. Superficial gas velocity in the commercial practice ranges from 20 to 90 meters/sec. The pressure drop of the gas stream through the reaction zone may be up to about 0.8 bar. The pressure drop and the air flow rate through the reactor are directly reflected in the energy requirement for the air compressor.

The most common versions of film reactors for commercial scale production consist either of a single annular conduit comprised of two cylindrical surfaces or of a plurality of round tubes associated together in a parallel (tube bundle) arrangement.

A major design feature of these systems is provision for even distribution of both feeds to the reactor. If this condition is not fulfilled, a greater quantity of SO_3 will react with the organic compounds on some portions than it will on other portions of the reactor, and "hot spots" may result in the early reaction stage in the areas where a too high excess of SO_3 is present. The resulting product would have poor color and a high free oil content. In addition, excessive amounts of organic mist, resulting from vaporization of low boiling constituents of the organic feed, and of SO_3, may leave the reactor with the exhaust gas. In an annular reactor tube, the most delicate point is getting uniform distribution of the organic reactant on the inner and outer reaction surfaces. It is also important that the two reaction surfaces be precisely concentric to help ensure uniform distribution of the SO_3. The distribution problem is increased

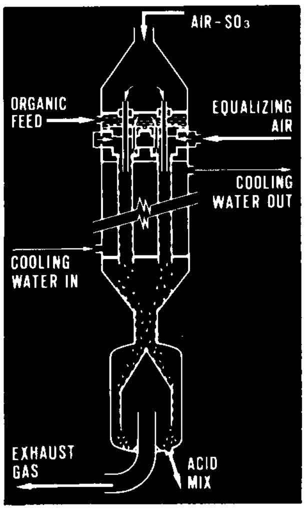

FIG. 5. Mazzoni reactor.

in a multi-tube reactor since equal metering to each tube is necessary to ensure even reaction in all tubes. Such operation can be difficult owing to possible differences in the pressure drops within the tubes arising from small differences in tube geometry, interface roughness, liquid flow rate, heat transfer rate, etc. Because of the competitive flow of gas and liquid, any increase in liquid flow rate or in liquid viscosity tends to reduce the cross-sectional area available for the gas flow.

The first commercial film sulfonation process was placed in operation by Stepan Chemical Company (11, 12). In this process, the organic feed is distributed to a plurality of externally cooled tubes and caused to flow on the inner surfaces of the tubes. The air-SO_3 is distributed through nozzles centrally located in the tubes and producing a discharge pressure drop which is high compared with the tube back pressure. Turbulence is induced in the film by impinging it with the air-SO_3 stream which discharges at high velocity from the nozzle. Film turbulence is effected simultaneously with controlled reduced film viscosity and heat exchange to rapidly dissipate the heat of reaction.

Allied: The reactor (Fig. 3) used for the Allied process (13, 14) consists essentially of two concentric water jacketed cylinders about 6 meters high and adapted to form an annular chamber in the space provided between the inner and outer reaction surfaces.

In the upper section of the reactor the organic feed is distributed and deposited as a film on the inner and outer reaction surfaces through two small peripheral slots extending around the entire reactor. About 4% air-SO_3 is introduced above the organic feed inlets and flows between the two organic moving films. At the bottom the acid mix is separated from the exhaust gas stream.

The capacity of a given reactor is determined by the diameter of the concentric cylinders in the reaction zone. The profile of the reaction zone is the same regardless of capacity.

The plant may be equipped with a sensing device which controls the amount of SO_3 entering the reactor.

A cost and profitability estimation for Allied units of medium capacity has been published (15).

Chemithon: The reactor system (Fig. 4) for the Chemithon film process (16-18) consists of two water jacketed cylinders about 1 meter long, one inside the other with a narrow annulus in between. A cage rotor turning in the upper section of the reaction zone provides for distribution of the organic feed on the inner and outer reaction surfaces and intensive mixing of the fresh reactants to avoid localized over-reaction. The reaction progresses in the remaining section of the reactor where the gas stream flowing at a high velocity intimately contacts the liquid reactant in the narrow gap between the walls.

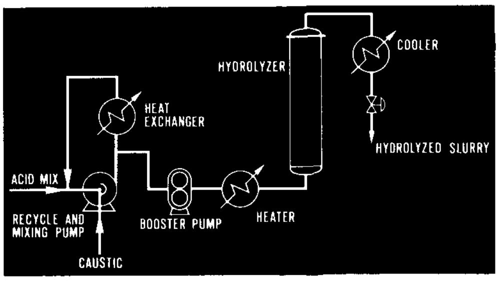

FIG. 6. Hydrolysis of alpha olefin sulfonates.

The heat evolved in the reaction is removed in part in the reactor and in part immediately after leaving the reaction zone by contacting the reaction mixture with cooled reaction product. The gas-liquid mixture leaves the reactor as a fog and goes to a cyclone for gas-liquid separation. Acid mix disengaged in the cyclone is pumped through a heat exchanger and back to the quenching section of the reactor. A slip stream of the acid proceeds to further processing.

The process uses SO_3 of about 4% strength. Here again the diameter of the reactor determines its capacity.

In this process, two reactors may be arranged in parrallel to discharge in a common recycle bath.

Mazzoni: The Mazzoni process (19) is based upon a multitube reactor with provision for pressure equalization. The reactor (Fig. 5) consists of water-cooled tubes about 2.5 meters long. It comprises a single feed chamber for the air-SO_3 and a single feed chamber for the organic raw material. Both feeds are distributed to the tubes by means of metering nozzles. The organic feed is deposited as a film on the inner surface, and the air-SO_3 is introduced in the central zone of each tube.

Through the annular openings surrounding the air-SO_3 nozzles, the tubes communicate with another single chamber, from which additional dry air or "equalizing air" can enter the tubes. Since the entrance pressure drops are only small fractions of the pressure drop in the air-SO_3 distributing nozzles, the equalizing air actually is distributed to the tubes in different fractional streams to match the differences in the pressure drops within the tubes and hence substantially to equalize the pressures downstream of the distributing nozzles for the gaseous and liquid reactants. This ensures a correct distribution of the reactants to the reactor tubes without limiting the pressure drop, and hence the energy input, therein.

As inherent features of this process, the streams of equalizing air entering the tubes between the air-SO_3 streams and the organic films provide an additional resistance to the mass transfer in the gas phase in the early reaction stage and shield the organic distribution system from SO_3 thus preventing accumulation of charred organic material.

The reaction mixture leaving the reactor tubes passes to a gas-liquid separator.

The air-SO_3 as it leaves the distributing nozzles and becomes diluted by the "equalizing air" may be up to about 6%.

The number of tubes determines the capacity of the reactor.

Spray Processes

Other approaches to the problem of achieving a quick uniform contact of the reactants involve reaction of the organic liquid in form of a mist with air-SO_3. Heat removal is provided by an additional air stream and/or by cooling the reaction product on heat transfer surfaces.

The Chemithon Corp. recently introduced the so-called "impact Jet Reactor" (20), a small unit in which the organic liquid in an atomized form is contacted with a high velocity stream of air-SO_3. The residence time in the contacting device is exceedingly short, and the resulting mixture is immediately cooled in a heat exchanger. The reaction mixture leaving the heat exchanger is passed to a gas-liquid separator. Concentrated air-SO_3 up to 8% may be used in this process.

A number of other equipment and processes for continuous sulfonation and sulfation with air-SO_3 have been disclosed in the patent literature. However, information as to their commercial utilization is lacking.

PROCESSING OF VARIOUS FEEDSTOCKS

Fatty Alcohols and Their Ethoxylates

The acid sulfates of alcohols and ethoxylates are unstable and must be neutralized within a short time after leaving the sulfation step. Because sulfation is a reversible reaction, neutralization should be carried out in controlled conditions to avoid local zones of low pH or excessive elevation of temperature, which would cause hydrolysis. Neutralization of acid sulfates and of sulfonic acids with caustic requires adequate cooling to dissipate the heat of reaction.

A conventional continuous neutralizer consists of a centrifugal pump connected to a heat exchanger with relatively short circulating piping. The pump serves a dual purpose for circulating a large volume of neutralized product and for acting as a mixer to disperse the streams of acid mix and alkali into the recirculating stream. The alkali is added through a valve or pump actuated by a pH controller. In making concentrated products, a positive displacement pump is required for circulating the slurry, and a mixer is inserted in the circulating line to produce intensive mixing action at the stage where the fresh reactants are introduced. Usually, the product is neutralized within the pH range of 7 to 8.5, and a buffer is added to prevent pH drift to the acid side (21, 22).

Alkylbenzenes

By-product sulfonic acid anhydride formation occurs in sulfonation of detergent alkylate with air-SO_3 (23). Digestion of acid mix is a standard procedure for completing the sulfonation reaction by reacting the free oil with anhydrides and dissolved SO_3 remaining in the liquid. The digestor may be a multistage stirred tank or a plug flow type reactor to provide a residence time of 5 to 15 min. The acid mix then goes to a hydrator where a small amount of water is added to completely decompose any residual anhydride. The hydrator is merely an inline mixer provided with cooling means to control the temperature of the acid mix during water addition. The stream leaving the hydrator is ready for storage or neutralization.

Cosulfonation of toluene or xylene with detergent alkylate provides an economical way of giving the proper proportion of hydrotrope in the finished product. Different approaches are used. Practical test runs on a large scale have been made in a Ballestra unit by feeding toluene to the last reaction stage (24). Cosulfonation of alkylate and xylene in a Chemithon film unit has been reported (17). Apparently, the major part of xylene is fed to the sulfonation reactor with the alkylate and a minor part after a first digestion stage to react with residual sulfonic acid anhydrides. Mixtures of alkylate and toluene or xylene have been cosulfonated in a Mazzoni plant.

Cosulfonation of alkylbenzene with fatty alcohols or alcohol ethoxylates is an alternative method to the post-blending of the neutralized salts. In the Ballestra process, the sulfatable organic may be introduced in one of the downstream sulfonating vessels. In the Chemithon film process, two parallel reactors are used. The sulfated product is underreacted but then digested with sulfonated acid containing sulfonic acid anhydrides to complete the reaction.

Alpha Olefins

Several reports and reviews have appeared on the technology of alpha olefin sulfonation, reaction mechanisms, and product composition (25-28). Most of the problems related to the very vigorous reaction of olefins with SO_3 have been eliminated with the use of short time reactors along with a low concentration of SO_3 in the gaseous mixture. The acid sulfonation products that are obtained from these units contain as major components alkene sulfonic acids and sultone inner esters. Alkaline hydrolysis converts the sultones to alkene monosulfonates and hydroxy alkane monosulfonates. Sultones undergo isomerization reactions (enlargement of the cyclic group) in the acid mix. Beta sultones give, by hydrolysis, the low soluble 2-hydroxysulfonates. However, beta sultones isomerize rapidly to gamma sultones and may be eliminated by digestion of the acid mix for a few minutes. Prolonged digestion time causes the gamma sultones to isomerize to delta sultones which are more difficult to hydrolyze.

Hydrolysis is best carried out in a continuous plug flow type reactor at about 150 C to obtain complete decomposition of sultones with a residence time of less than 30 min. In the neutralization step (Fig. 6), added to the acid mix is a slight excess of caustic based on the amount required to neutralize the sulfonic acid initially present and that formed in the subsequent hydrolyzing step. The temperature is controlled in the neutralization step to maintain the slurry in fluid condition. The slurry is then pumped to the hydrolyzer through a preheater. The temperature of the slurry leaving the hydrolyzer is lowered in an after-cooler. In most cases a final bleaching is required to make sulfonate of acceptable color. Bleaching is usually done with sodium hypochlorite in a semibatch operation.

Patents describe production of detergent alpha olefin sulfonates in integrated continuous processes (29, 30).

Fatty Acids and Esters

Contribution to the technical sulfonation of saturated fatty acid esters with air-SO_3 given at Henkel & Cie GmbH have been reported (31, 32). The reaction of SO_3 with fatty esters, such as methyl esters, proceeds in two steps. The first step is rapid adduct formation between SO_3 and the ester group. The second step is a slow, temperature dependent sulfonation in alpha position.

The technical sulfonation process may be carried out either with a multistage cascade reactor (Ballestra) or by using a short-time reactor with an additional stage for an extended residence time reactor. A bleaching procedure has been developed which basically consists of treating the sulfonate with hydrogen peroxide before neutralization under controlled conditions of acidity and temperature. The danger of ester hydrolysis in the subsequent neutralization is small if pH and temperature are adequately controlled. Fatty acids may be sulfonated under about the same conditions of the fatty esters.

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