



# Sulfonation and Sulfation Processes

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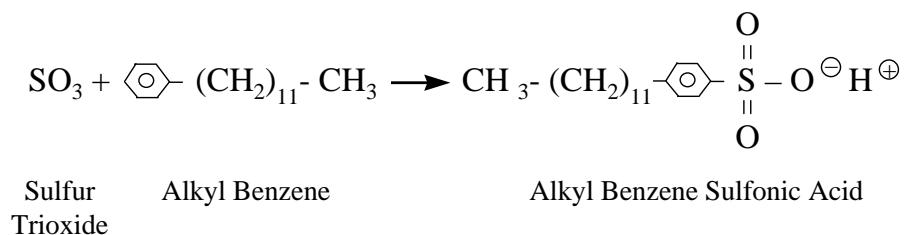
### Introduction

Sulfonation and sulfation are major industrial chemical processes used to make a diverse range of products, including dyes and color intensifiers, pigments, medicinals, pesticides and organic intermediates. Additionally, almost 500,000 metric tons per year of lignin sulfonates are produced as a by-product from paper pulping. Petroleum sulfonates are widely used as detergent additives in lubricating oils. However, the majority of the 1.6 million metric tons of sulfonates and sulfates produced annually in the United States<sup>[1]</sup> are used as surfactants in laundry and consumer products applications. This chapter focuses only on commercial techniques for production of detergent range sulfonates and sulfates.

### Basic Chemistry

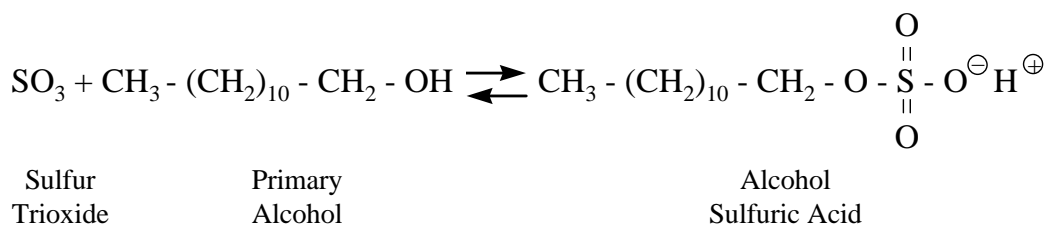
Although sulfonates and sulfates are similar in structure, there are important differences. Figure 1 shows the reaction to produce a sulfonate. Sulfur trioxide (SO<sub>3</sub>) reacts with an organic molecule – in this case an alkyl benzene – to form a sulfur-carbon bond. One of the characteristics of this process is that the resultant alkyl benzene sulfonic acid is a stable molecule.

**Figure 1. Sulfonation**



Sulfation, on the other hand, involves forming a carbon-oxygen-sulfur bond as shown in Figure 2. The resultant alcohol sulfuric acid is not hydrolytically stable. Unless neutralized, it decomposes to form sulfuric acid and the original alcohol.

**Figure 2. Sulfation**



Because they are stable, sulfonic acids can be isolated, stored and shipped as an article of commerce. Sulfates, due to their instability, are available only as neutral compounds. This stability difference in the products of reaction with SO<sub>3</sub> also has a profound impact on the choice of process used to produce sulfonates or sulfates. Some processes, such as oleum sulfonation, cannot be used to make alcohol sulfates containing a low level of inorganic sulfate. However others, such as sulfamic acid sulfation, cannot be used to make sulfonic acids.

SO<sub>3</sub> is an aggressive electrophilic reagent that rapidly reacts with any organic compound containing an electron donor group. Sulfonation is a difficult reaction to perform on an industrial scale because the reaction is rapid and highly exothermic, releasing approximately 380 kJ/kg SO<sub>3</sub> (800 BTUs per pound of SO<sub>3</sub>) reacted<sup>[2]</sup>. Most organic compounds form a black char on contact with pure SO<sub>3</sub> due to the rapid reaction and heat evolution. Additionally, as shown in Figure 3, the reactants increase in viscosity between 15 and 300 times as they are converted from the organic feedstock to the sulfonic acid<sup>[1]</sup>. This large increase in viscosity makes heat removal difficult. The high viscosity of the formed products reduces the heat transfer coefficient from the reaction mass.

**Figure 3. Viscosity Increase on Sulfonation**

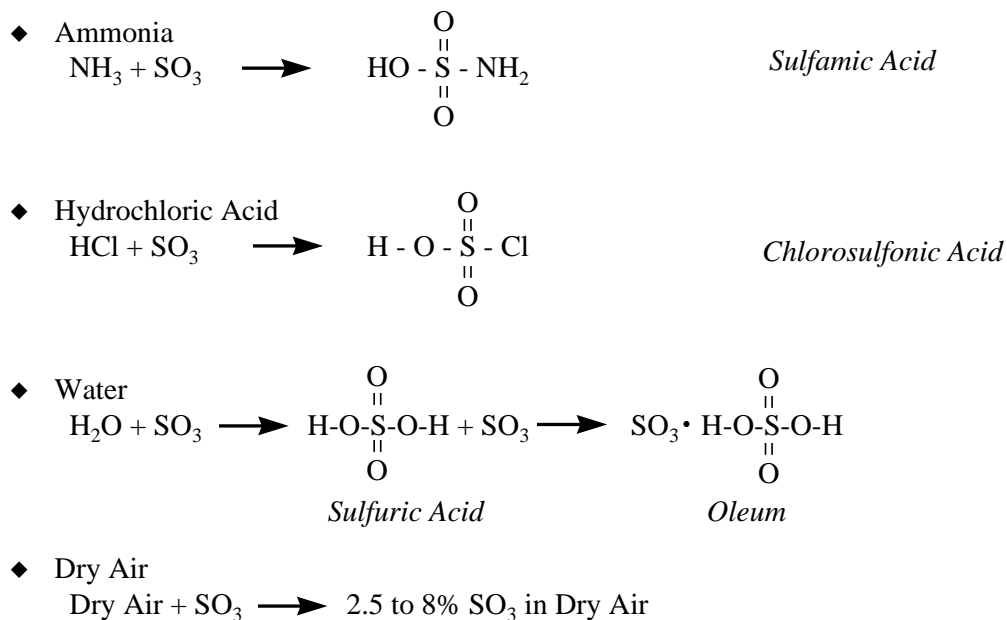
Feedstock	Feed Viscosity (cp)	Acid Viscosity @ 40 - 50°C
Linear alkyl benzene	5	400
Branched alkyl benzene	15	1000
Ethoxylated alcohol	20	500
Tallow alcohol	10	150
Alpha olefins	3	1000

Effective cooling of the reaction mass is essential because high temperatures promote

side reactions that produce undesirable by-products. Also, precise control of the molar ratio of SO<sub>3</sub> to organic is essential because any excess SO<sub>3</sub>, due to its reactive nature, contributes to side reactions and by-product formation. Therefore, commercial scale sulfonation reactions require special equipment and instrumentation that allows tight control of the mole ratio of SO<sub>3</sub> to organic and rapid removal of the heat of reaction.

Historically, the problem of SO<sub>3</sub> reactivity has been solved by diluting and/or complexing the SO<sub>3</sub> to moderate the rate of reaction. Commercially, the diluting or complexing agents (Figure 4) include ammonia (sulfamic acid), hydrochloric acid (chlorosulfuric acid), water or sulfuric acid (sulfuric acid or oleum) and dry air (air/SO<sub>3</sub> film sulfonation). Control of the ratio of SO<sub>3</sub> to organic raw material is vital to achieving the desired product quality with use of any of the agents. Additionally, these processes require heat removal to maintain product quality. As we examine each of these industrial processes we will see how they have been engineered to achieve these requirements.

**Figure 4. Agents to Reduce SO<sub>3</sub> Reactivity**

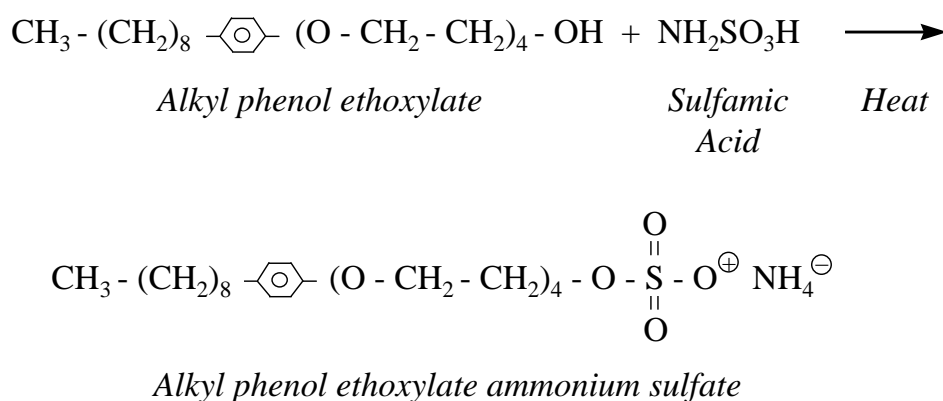


### **Commercial Sulfonation Processes**

Sulfamic acid (NH<sub>2</sub>SO<sub>3</sub>H) is used to sulfate alcohols and ethoxylated alcohols to form an ammonium neutralized salt. A typical reaction is shown in Figure 5. The reaction goes

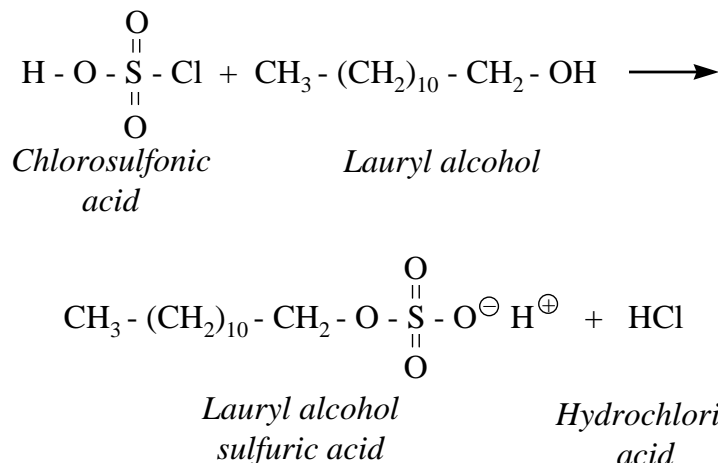
directly to the ammonium salt of the alcohol sulfuric acid. Sulfamic acid is an expensive reagent, costing approximately US\$0.51 per pound of reactive SO<sub>3</sub>. Sulfamic acid sulfation is a mild and specific sulfating reagent suitable for making ammonium neutralized alcohol ethoxylates. Another major advantage of sulfamic acid is that it selectively sulfates alcohol groups and will not sulfonate aromatic rings. Therefore, its major use is sulfation of alkyl phenol ethoxylates. This specificity prevents formation of mixed sulfate-sulfonate compounds. Sulfamic acid is easily handled and reacts stoichiometrically with the alcohol or ethoxy alcohol. It readily adapts to making small quantities of material in low cost batch equipment.

**Figure 5. Sulfamic Acid Sulfation**



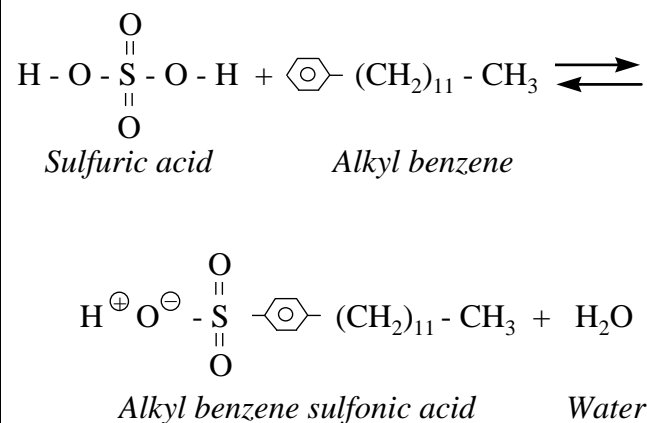
Chlorosulfuric acid (ClSO<sub>3</sub>H) is also widely used to produce alcohol sulfates, alcohol ether sulfates, dyes and dye intermediates. Figure 6 shows a typical reaction. Note that as the reaction moves to completion, hydrochloric acid (HCl) is released. This acid must be scrubbed or otherwise recovered. Chlorosulfuric acid is an expensive source of SO<sub>3</sub> although it is approximately one half the cost of sulfamic acid. The cost per pound of reactive SO<sub>3</sub> is US\$0.255. It is a rapid, stoichiometric reactant. However, it is still more expensive than other sources of SO<sub>3</sub>. It is also corrosive and a hazardous chemical to handle and liberates HCl as a by-product during the reaction. The HCl can be recovered by scrubbing the off-gas stream with water, or neutralized by scrubbing the off-gas with a dilute basic scrubbing solution. In either case, additional equipment and complexity are added to the process.

**Figure 6. Chlorosulfonic Acid Sulfation**



Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and oleum (SO<sub>3</sub> • H<sub>2</sub>SO<sub>4</sub>) are widely used as sulfonating agents. Oleum is used to sulfonate alkyl benzene and sulfate fatty alcohols for heavy duty detergents. The reaction is shown in Figure 7. It is an equilibrium process, as water is formed in the reaction and the resultant water dilutes the oleum and/or sulfuric acid. The sulfonation reaction stops when the sulfuric acid concentration drops to approximately 90%. This "spent" acid may be separated from alkyl benzene sulfonic acid to produce a product, which on neutralization contains a relatively low level (6-10%) of sodium sulfate. When fatty alcohols are sulfated, the spent acid cannot be separated. It must be neutralized with the alcohol sulfuric acid to make a product containing a high level of sodium sulfate. Oleum is relatively inexpensive – about US\$0.153 per pound of reactive SO<sub>3</sub>. Oleum sulfonation can be operated as either a batch or continuous process. This process has the dual advantage of low SO<sub>3</sub> cost and low capital equipment cost. However, it has the disadvantage of being an equilibrium process which leaves large quantities of un-reacted sulfuric acid. This

**Figure 7. Sulfuric Acid / Oleum**

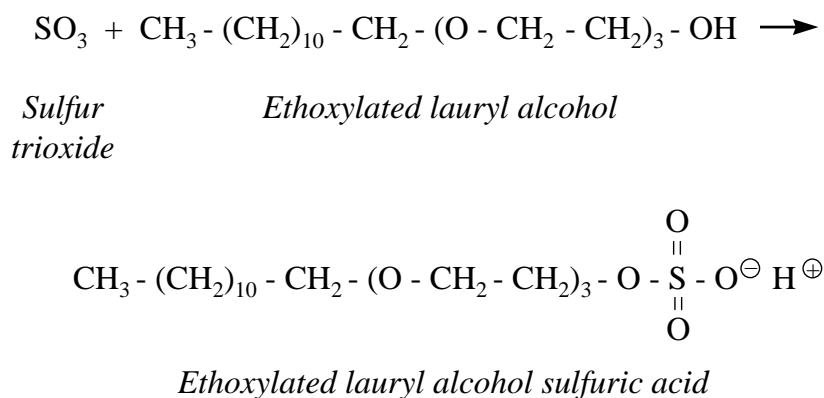


waste acid must be separated from the reaction mixture and subsequently disposed. In North America, the expense of disposing the "spent" sulfuric acid has become so high that the process economics are now questionable.

Sulfonation with sulfuric acid is a special case of oleum sulfonation. Because the sulfonation reaction stops when the acid concentration in the reaction mixture drops to less than approximately 90%, sulfonation of detergent feedstocks with sulfuric acid is not normally practiced. Today sulfuric acid sulfonation is principally used for production of hydrotropes by azeotropic reaction with benzene, toluene or xylene. In this special process, the water formed during the reaction is removed by azeotropic distillation of the water and unreacted feedstock. The water is then separated from the immiscible organic feedstock which is returned to the reaction vessel. Because water is removed, the reaction may continue to completion.

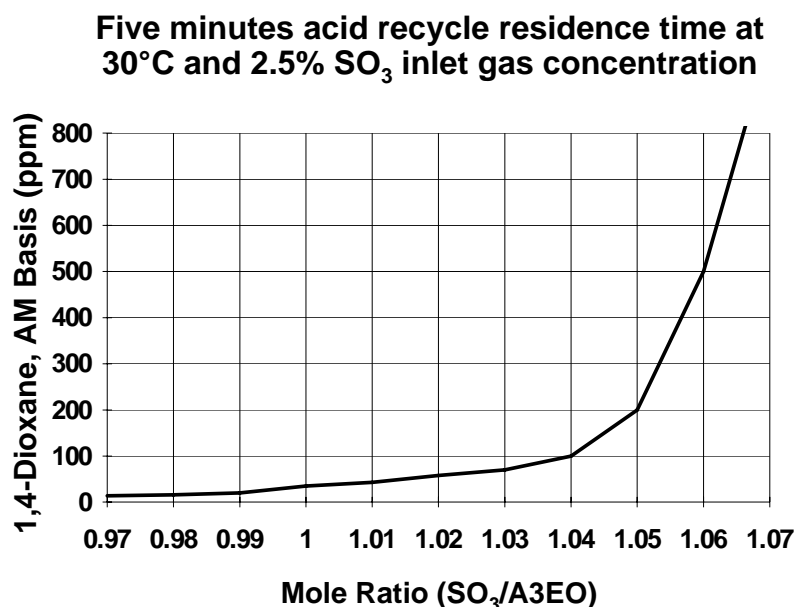
The air/SO<sub>3</sub> sulfonation process is a direct process in which SO<sub>3</sub> gas is diluted with very dry air and reacted directly with the organic feedstock. The source of the SO<sub>3</sub> gas may be either liquid SO<sub>3</sub> or SO<sub>3</sub> produced by burning sulfur. As shown in Figure 8, the reaction of gaseous SO<sub>3</sub> with organic is rapid and stoichiometric. It is complicated by the possibility of side reactions and therefore tight process control is essential. The cost for liquid SO<sub>3</sub> is US\$0.09 per pound of reactive SO<sub>3</sub>; while SO<sub>3</sub> from sulfur burning is US\$0.02 per pound of reactive SO<sub>3</sub>. The air/SO<sub>3</sub> sulfonation process is the lowest SO<sub>3</sub> cost of any sulfonation process and is extremely versatile, producing very high quality products. However, it is a continuous process best suited to large production volumes. In addition, it requires expensive precision equipment and highly trained operating personnel.

**Figure 8. Air / SO<sub>3</sub>**



As previously mentioned, a commercially successful sulfonation process requires reaction of  $\text{SO}_3$  with the organic feedstock under tightly controlled conditions. Figure 9 illustrates the level of control demanded by the air/ $\text{SO}_3$  sulfonation process<sup>[3]</sup>. This illustration shows the production of 1,4-dioxane, an undesirable by-product formed during the sulfonation of ethoxylated alcohols. The 1,4-dioxane formed is a function of mole ratio (kg moles per unit time of  $\text{SO}_3$  fed to the reactor divided by kg moles per unit time of feedstock fed to the reactor). As the mole ratio of  $\text{SO}_3$  to organic feedstock increases, the level of dioxane in the product remains relatively low at 20 to 30 ppm. A critical point of over-sulfation occurs at a mole ratio of approximately 1.03. Once over-sulfation occurs and the mole ratio exceeds 1.04, dioxane production increases rapidly to values measured in hundreds of parts per million. Similar adverse responses are observed with product color or levels of unsulfonated or unsulfated (free oil) materials in the product. Clearly, the sulfonation process must be controlled to within 1% of the desired mole ratio in order to achieve excellent product quality. Other important process variables are reaction temperature,  $\text{SO}_3$  gas concentration, time to neutralization, neutralization pH and neutralization temperature. These variables also influence product quality although the effect is not as dramatic as the effect of mole ratio.

**Figure 9. 1,4-Dioxane vs. Mole Ratio**







The profound effect of mole ratio on product quality implies that an air/SO<sub>3</sub> sulfonation reactor must be designed to ensure the mole ratio is equally and constantly maintained at all points in the reactor. I have coined the phrase "micro scale" mole ratio control to describe this condition. Micro scale control means that the reactor has been designed and calibrated so that the same mole ratio is held constant at every point at a cross section through the linear flow axis of the reactor. All molecules of feed see exactly the same quantity of SO<sub>3</sub>. This is different than the macro mole ratio control which is the overall mole ratio of organic feedstock and SO<sub>3</sub> fed to the reactor. Macro control is determined by the plant's control system. It is imperative that the equipment be capable of both macro and micro mole ratio control because sulfonation is such a critical reaction with respect to mole ratio control. A 1% variation in the mole ratio can spell the difference between world class product and off-specification material.

### ***Choosing a Sulfonation Process***

The choice of sulfonation process depends on many factors. One of the most important is the desired products and their required quality. Some processes are very versatile while others produce only a few types of products. Each process produces slightly different products. For example, the sulfamic acid process produces only ammonium sulfates from alcohols or ethoxylated alcohols. Another example is the presence of a minimum of 8% sulfate in sodium alkyl benzene sulfonates made with oleum. Some processes such as the air/SO<sub>3</sub> process are capable of sulfating or sulfonating a wide variety of feedstocks and producing excellent quality products from all of them.

A second factor to consider in the choice of sulfonation process is the required production capacity. The sulfamic acid process is a batch process suitable for production of small quantities of material. The air/SO<sub>3</sub> process is a large scale continuous process best suited to 24 hours per day, seven days per week manufacture of tons per hour of product. The chlorosulfuric acid and oleum processes can be run as either batch or continuous processes.

Reagent cost may have a major impact on choosing a process. The air/SO<sub>3</sub> process has the lowest cost per pound of SO<sub>3</sub> reacted while the sulfamic acid process has the highest. For large scale commodity production, the air/SO<sub>3</sub> process clearly has an advantage. However, for small scale production of a high value specialty product this advantage may be outweighed by other considerations such as initial equipment cost and the necessity for continuous operation.

The process equipment cost is an important factor to be considered in choice of a sulfonation process. You must look at the installed cost of the system, tankage and required safety systems. The equipment cost is almost exactly the inverse of the reagent cost. Here, the air/SO<sub>3</sub> process is highest in cost while the simple batch sulfamic process is lowest. Other processes are intermediate.

The final factor to consider in the choice of sulfonation processes is the cost of waste disposal. The chlorosulfuric acid and oleum sulfonation processes produce large by-product streams of either hydrochloric acid or sulfuric acid. These by-products must be recovered and sold, or disposed of as a waste. Waste disposal can have a significant impact on the profitability of these processes, as the necessary equipment can be costly and the disposal costs can be high.

Figure 10 shows the trends in sulfonation plants in the United States<sup>[1]</sup>. The air/SO<sub>3</sub> process has rapidly overtaken the oleum process as the predominate choice. This is the result of several trends. The first is the waste disposal cost for the spent sulfuric acid from the oleum process. The second is the desire of many processors to avoid storing a hazardous material such as oleum. The third is the move toward compact detergent products which reduces or eliminates the sodium sulfate content of detergent products. The oleum process adds a large quantity of sulfate to the products and for many applications this is not acceptable. Finally, the air/SO<sub>3</sub> process is capable of making a broad range of very high quality products.

**Figure 10. Estimated U.S. Sulfonation Plants**

Plant Type	1980		1985		1990	
	No. of Plants	Capacity*	No. of Plants	Capacity*	No. of Plants	Capacity*
SO <sub>3</sub>	44	630.0	62	855	41	1,016
Oleum	51	720.0	50	605	39	548
Chlorosulfonic Acid	5	35.0	6	50	6	59
Sulfoxidation	1	0.45	2	1.35	1	0.45
<b>Totals</b>	<b>101</b>	<b>1385.45</b>	<b>120</b>	<b>1,511.35</b>	<b>87</b>	<b>1,623.45</b>

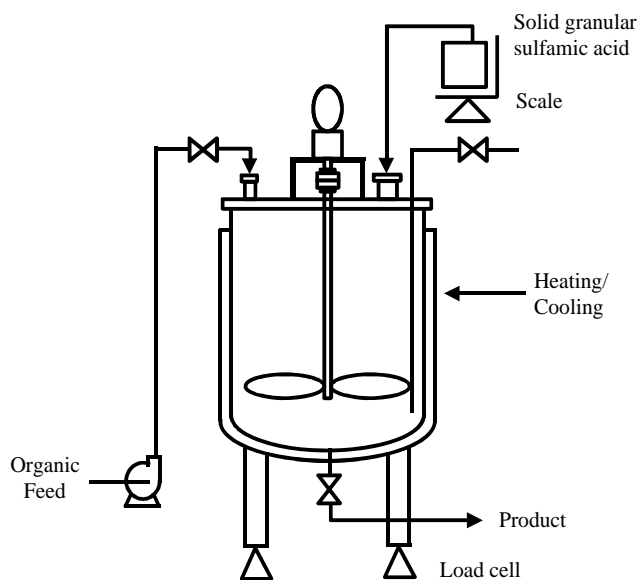
\*Million kg/yr (*Information supplied by E.A. Knaggs*)

## **Commercial Scale Sulfonation Equipment**

### **Sulfamic Acid Sulfation Equipment**

Figure 11 illustrates the equipment used for sulfamic acid sulfation. This batch process is run in a stainless steel or glass lined, air tight, stirred tank reactor. The reactor has heating and cooling coils and provision for weighing in the organic reactant and the sulfamic acid. Before the reaction starts, air is purged from the reactor with dry nitrogen and the reaction is run under a blanket of nitrogen. The organic is weighed into the reactor and a 5% molar excess of sulfamic acid is then added. The reactor is purged and blanketed with dry nitrogen to remove oxygen. The reactants are heated to 110–160°C and held at this temperature for approximately 90 minutes. The products are then cooled to 70°C and water or alcohol are added to dilute the product. As previously mentioned, an ammonium salt is the direct reaction product so no neutralization step is required.

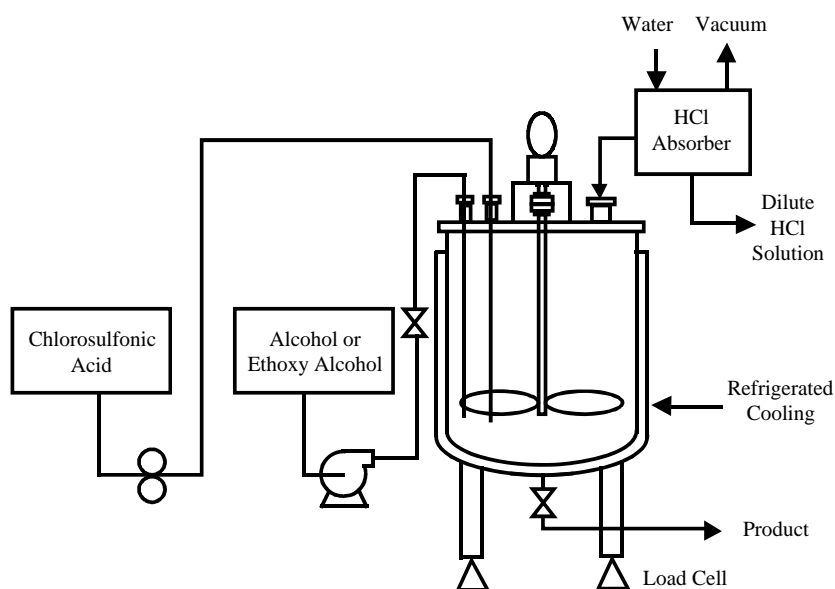
**Figure 11. Sulfamic Acid Sulfation**



## Chlorosulfonic Acid Sulfation Equipment

Chlorosulfuric acid can be used to sulfonate in either a batch or continuous process. For the batch process, illustrated in Figure 12, the equipment is a glass lined, stirred, sealed reactor with heating and cooling jackets. The reactor must be fitted with a glass lined absorber to remove the HCl gas evolved in the reaction. A slight vacuum is usually pulled on the reaction vessel to enhance HCl removal. The liberated HCl gas is absorbed into water to make a dilute HCl solution. In operation, the alcohol or ethoxy alcohol feedstock is charged to the reactor and chlorosulfuric acid is gradually added. A good refrigeration system is required for heat removal because the reaction is exothermic. The reaction mass must be kept at approximately 25°C to avoid side reactions and color body formation and to minimize foaming. The rate of addition of chlorosulfuric acid is adjusted to ensure that this temperature is not exceeded. Immediate neutralization is required once the reaction is complete.

**Figure 12. Batch Chlorosulfonic Acid Sulfation**



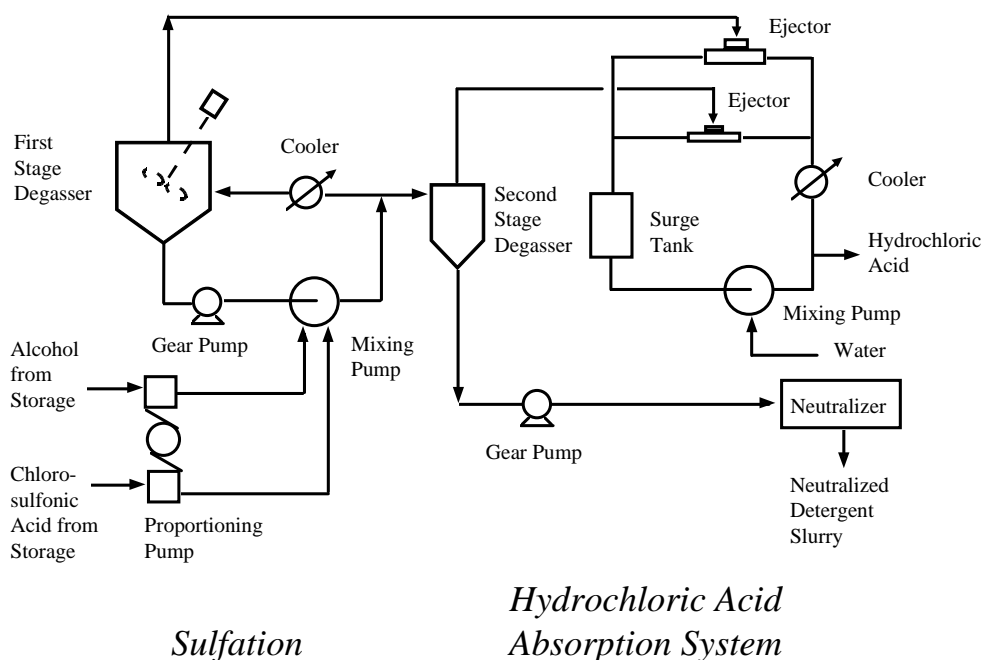
Chlorosulfation can also be continuous. Figure 13 shows a typical flow sheet for a continuous chlorosulfuric acid sulfation process. In this application the alcohol and chlorosulfuric acid are added into a mixing zone, combined and sent to a degasser. A slight vacuum is pulled on the degasser to assist separation of HCl from the reaction products. The disengaged sulfonic acid is sent through a heat exchanger to remove the heat of reaction and recycled back to the mixer to cool the process. A portion of the

reaction mixture is sent to a second degasser where the HCl separation is completed. The HCl is continuously absorbed into water and the acid mixture is continuously neutralized. Several companies including Henkel use continuous chlorosulfation technology for making detergent actives. The process is economically viable if a source for the HCl is available and if the product, which contains some residual chloride ion, is acceptable.

### Oleum and Sulfuric Acid Sulfonation Equipment

Oleum and sulfuric acid can be used to sulfonate aromatics and alcohols in either batch or continuous equipment. For detergent alkylates, the batch equipment is very similar to other processes. As shown in Figure 14, the required equipment is a stirred, sealed, glass lined or stainless steel kettle with a provision

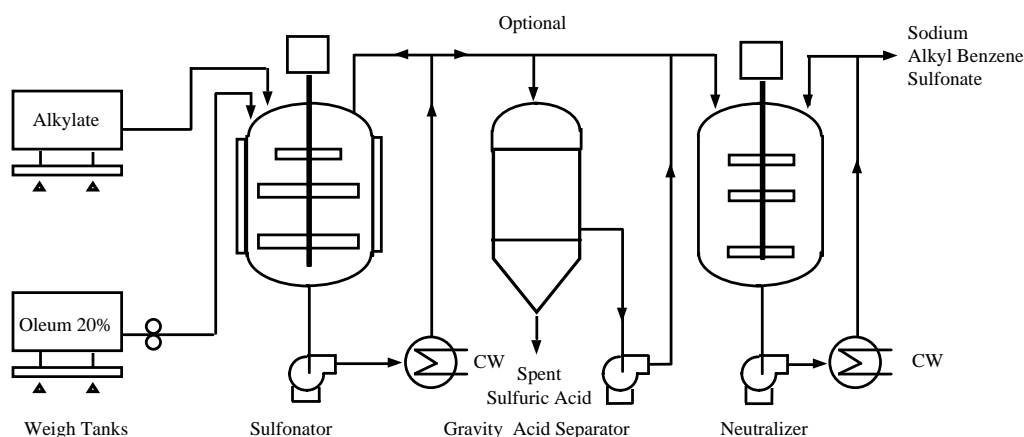
**Figure 13. Continuous Alcohol Sulfation with Chlorosulfonic Acid**



for heating and cooling. The detergent alkylate is first added to the reaction vessel then the oleum is slowly added over a period of several hours. The reaction is highly exothermic and the oleum addition rate is determined by the ability to remove the heat of reaction. The temperature should be maintained below 35°C for optimum product quality. Frequently the heat of reaction is removed by pumping the reaction mixture

through an external heat exchanger. Because it is an equilibrium reaction, except for the special case of azeotropic sulfonation of hydrotropes with sulfuric acid, a large surplus of sulfuric acid forms. When the sulfonation reaction is complete, the sulfuric acid may be separated from the sulfonated detergent alkylate by adding water. The water addition (typically about 10% by weight of the reaction mixture) causes a phase separation to occur between the sulfonic acid and the diluted sulfuric acid. The separation usually takes place in a separate, glass lined vessel and occurs over a period of about

**Figure 14. Batch Oleum Sulfonation of Detergent Alkylate**

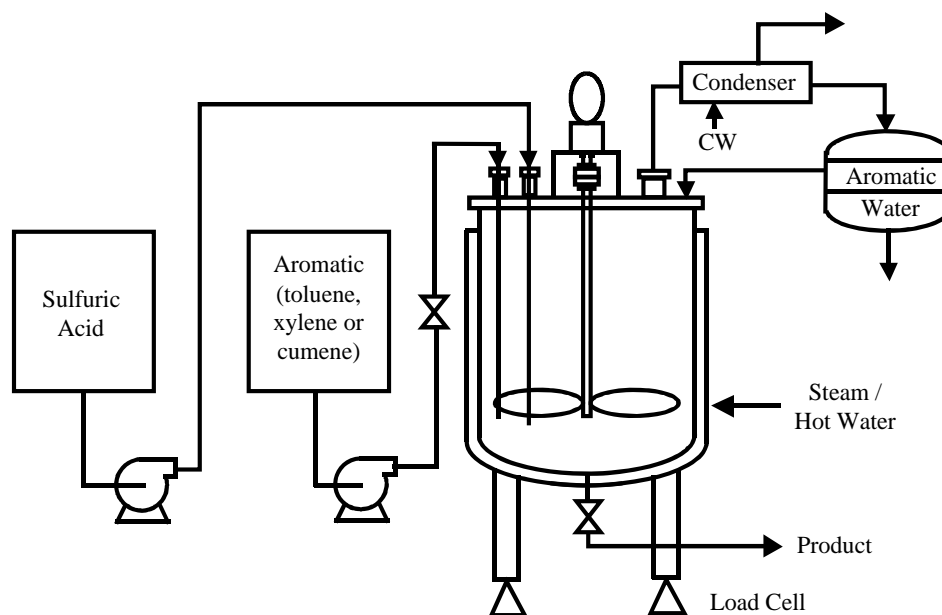


10 hours. Materials of construction are crucial because the dilution process makes sulfuric acid which is in a very corrosive temperature and concentration range. After separation, the sulfonic acid may be neutralized with aqueous sodium hydroxide, usually in a separate neutralization vessel. Including neutralization, total batch time is 15 to 20 hours. The product contains about 15% sodium sulfate after neutralization if the acid is separated, and about 60% sodium sulfate if not. Without separation, the product's application is limited to low active, traditional detergent powders where the large content of sodium sulfate is used as a filler.

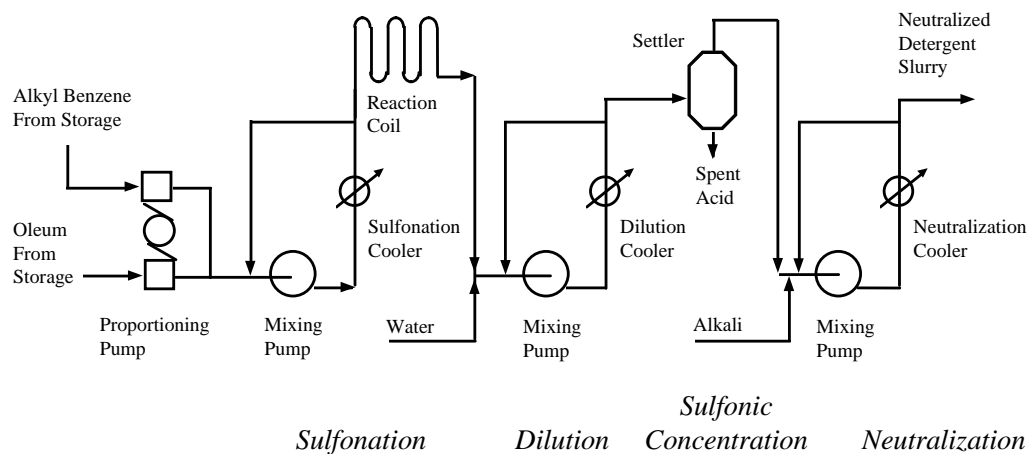
In the special case of azeotropic sulfonation of toluene, cumene or xylene with 98% sulfuric acid to form hydrotropes, a reflux condenser is added at the top of the reactor. The condenser separates the unreacted feed from the water produced in the reaction. The water is removed from the condenser, and the feed is refluxed back to the reactor. Because the water is removed, the reaction proceeds to completion and a large excess of sulfuric acid is not required. Typical equipment for hydrotrope sulfonation is shown in Figure 15.

The invention of the process for continuous oleum sulfonation was the foundation of The Chemithon Corporation in 1954<sup>[4, 5]</sup>. Figure 16 shows a flow sheet for continuous oleum sulfonation of detergent alkylate. In this process, alkyl benzene is mixed and reacted with oleum in a recycle loop where the reaction mixture is cooled by recycling it through a heat exchanger. Typical reaction temperatures in the recycle loop are 38–54°C. The mixed acid products

**Figure 15. Batch Azeotropic Sulfonation of Aromatics with Sulfuric Acid**



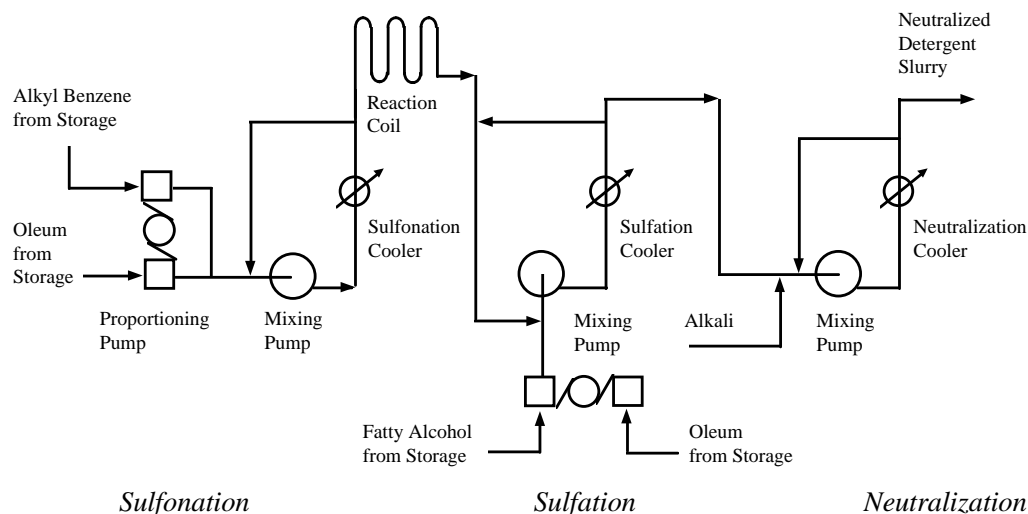
**Figure 16. Continuous High Active Alkylate Sulfonation with Oleum**



are digested in a plug flow reactor and then dilution water (approximately 13% by weight) is added in a second mixing loop. A second heat exchanger removes the heat of dilution. The diluted sulfuric acid and alkylbenzene sulfonic acid are separated in a continuous settler. The sulfonic acid is then continuously neutralized with aqueous sodium hydroxide solution in a third, cooled mixing loop. Sulfate levels as low as 10% in the final product can be achieved in this equipment. Total processing time is less than one hour. The equipment can also be used to sulfate detergent range alcohols for use in laundry powders if a high level of sulfate in the product can be tolerated. The sulfates are present because the separation process cannot be used when sulfating alcohols. If water is added to the alcohol sulfuric acid/sulfuric acid mixture, the alcohol sulfuric acid immediately hydrolyzes. Additionally, mixed products containing both alkyl benzene sulfonates and alcohol sulfates can be manufactured as shown in Figure 17. In this case alkylate is sulfonated first, followed by sulfation of the alcohol. Some of the excess sulfuric acid from the sulfonation stage is used to react with the alcohol and the combined mixture is immediately neutralized. Because no separation stage is used, the resultant product is high in sulfate.



**Figure 17. Continuous Tandem Type Sulfonation-Sulfation with Oleum**



### Air/SO<sub>3</sub> Sulfonation Equipment

Four possible sources of SO<sub>3</sub> gas used for an air/SO<sub>3</sub> sulfonation system are:

- Sulfuric acid plant converter gas
- SO<sub>3</sub> from boiling concentrated oleum
- Liquid SO<sub>3</sub>
- Sulfur burning in equipment specifically designed to produce SO<sub>3</sub> gas for sulfonation

Converter gas from a sulfuric acid plant contains 10–12% SO<sub>3</sub> and appears to be a potential SO<sub>3</sub> source for sulfonation. There are several problems with using a sulfuric acid plant as an SO<sub>3</sub> source for sulfonation. Nevertheless, such an arrangement has been commercially installed and at first glance appears to be an attractive, low cost method of supplying SO<sub>3</sub> gas to a sulfonation plant. Physical location is a limiting factor; as the sulfonation plant must be installed as closely as possible to the sulfuric acid plant converter. In addition, the sulfonation plant can run only when the sulfuric acid plant is running.

There are three other more subtle difficulties when using a sulfuric acid plant as an SO<sub>3</sub> source for sulfonation. First, the SO<sub>3</sub> gas at approximately 18% concentration must be diluted to the normal range for sulfonation (typically 4–7%). An auxiliary air supply must be installed, which adds expense and complexity. Second, because sulfuric acid absorption towers are used for air drying, the air/SO<sub>3</sub> from a sulfuric acid plant has a higher dew point (typically –35°C) than that required in a sulfonation plant (typically –



60°C to -80°C). The high dew point causes product quality problems in the sulfonation process and accelerates corrosion of the process equipment. Third, the pressure of the air/SO<sub>3</sub> from the sulfuric acid plant is usually not sufficient to overcome the pressure drop of the sulfonation system. Compressing the air/SO<sub>3</sub> from the converter is not trivial as it requires a high alloy compressor to withstand the corrosive environment created by the wet air/SO<sub>3</sub> stream. This problem can be overcome, but the solution is not inexpensive. Considering all the problems inherent in utilizing the converter gas stream from a sulfuric acid plant, the conclusion is that it is technically feasible. However this choice adds significant operational difficulties and does not result in a major cost savings over installing a complete sulfur burning sulfonation plant.

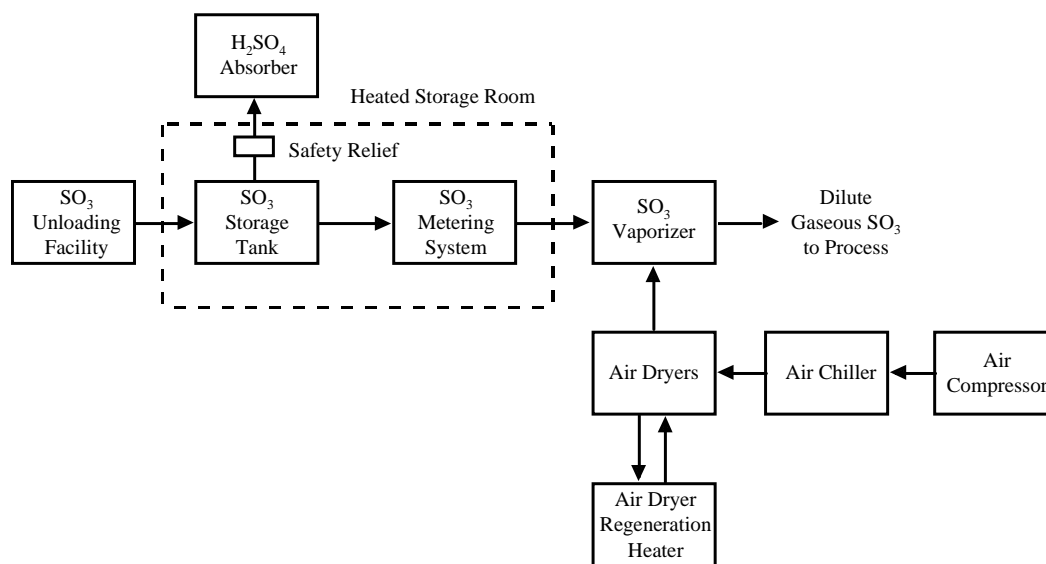
Another possible source of SO<sub>3</sub> for sulfonation is produced by boiling oleum to produce gaseous SO<sub>3</sub> which is then blended with dry air. It is practically limited to locations where fresh oleum can be received, and depleted oleum returned by pipeline. Compared to sulfur burning, this process somewhat reduces the equipment requirement. However, it still requires an air supply system, an oleum boiler and an SO<sub>3</sub> metering system. Unlike a sulfur burning plant which generates its own heat for air dryer regeneration, this air supply system requires an external source of heat which adds extra utility expenses. Also, significant safety hazards are associated with handling concentrated oleum. Such an installation may be economical for a few site locations, and at least one is commercially operating in North America.

Some of the first air/SO<sub>3</sub> sulfonation plants installed were based on use of liquid SO<sub>3</sub>. These plants require an air supply system identical to the system described below for a sulfur burning plant except that it also requires an external heat source for air dryer regeneration. In addition, a liquid SO<sub>3</sub> plant requires an SO<sub>3</sub> storage system. This storage system is usually a large 20,000 to 80,000 kg storage tank located in a heated room and maintained at a temperature of about 40–43°C. Heating the SO<sub>3</sub> storage room can be a significant cost in colder climates. In case of SO<sub>3</sub> leaks, the room must be sealed and should have provision for scrubbing any SO<sub>3</sub> that escapes into the room's atmosphere. In the sulfonation process, the liquid SO<sub>3</sub> is metered from the storage tank into a steam heated vaporizer where it is evaporated and mixed into the dried air stream from the air supply system. From this point on, the process is identical to a sulfur burning air/SO<sub>3</sub> sulfonation plant, described below. A liquid SO<sub>3</sub> storage and metering system is shown in Figure 18. Because of the rigorous storage requirements imposed by the hazardous nature of liquid SO<sub>3</sub>, the installed cost for a liquid SO<sub>3</sub> sulfonation facility is close to that for a sulfur burning installation.

There are significant safety advantages to a sulfur burning system. With sulfur burning air/SO<sub>3</sub> sulfonation processes, the only SO<sub>3</sub> on site is the small quantity of dilute gaseous material in the process piping between the converter (SO<sub>2</sub> to SO<sub>3</sub>) and the sulfonation

reactor. Even in the world's largest sulfonation plant (20,000 kg/hr active production), this amounts to only about 100 kg of dilute SO<sub>3</sub> gas. The sulfur burning process is much safer than transporting, storing and handling tank truck (18,000 kg) or rail car (72,000 kg) quantities of oleum or liquid SO<sub>3</sub>. Sulfonation equipment based on liquid SO<sub>3</sub> has become increasingly undesirable for the following reasons:

**Figure 18. Dilute SO<sub>3</sub> Gas from Liquid SO<sub>3</sub>**



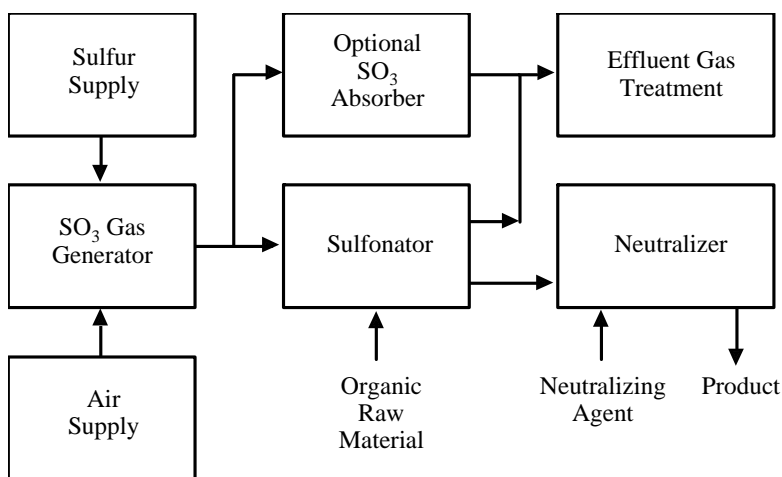
- Safety concerns
- Liquid SO<sub>3</sub> is unavailable in many parts of the world
- Sulfur is readily available worldwide
- Sulfur is relatively inexpensive

The remainder of this section, therefore, is confined to the description of a state of the art sulfur burning, air/SO<sub>3</sub> sulfonation plant.

The basic plant package for a sulfur burning, air/SO<sub>3</sub> sulfonation installation includes a sulfur supply system, air supply system, SO<sub>3</sub> gas plant system, SO<sub>3</sub> absorber system, sulfonator, neutralizer, effluent gas clean-up system, control system and motor control center. This system is shown as a block diagram in Figure 19. You can add additional equipment as required to manufacture specialty products, such as a hydrolyzer for alpha

olefin sulfonate production, re-esterification and bleaching equipment for methyl ester sulfonate production, dioxane strippers for production of ethoxy alcohol sulfates containing ultra low dioxane levels (less than 10 ppm), and dryers for producing concentrated, pure detergent active. Capacities for commercial sulfur burning air/SO<sub>3</sub> sulfonation units range from 250 to 20,000 kg/hr of 100% detergent active. Typically, an air/SO<sub>3</sub> sulfonation plant is designed to sulfonate with approximately 4–7% (volume) SO<sub>3</sub>. However, if you plan to use ethoxylated alcohol as a major feedstock, the SO<sub>3</sub> gas concentration may be as low as 2.75% SO<sub>3</sub> in air to the sulfation systems.

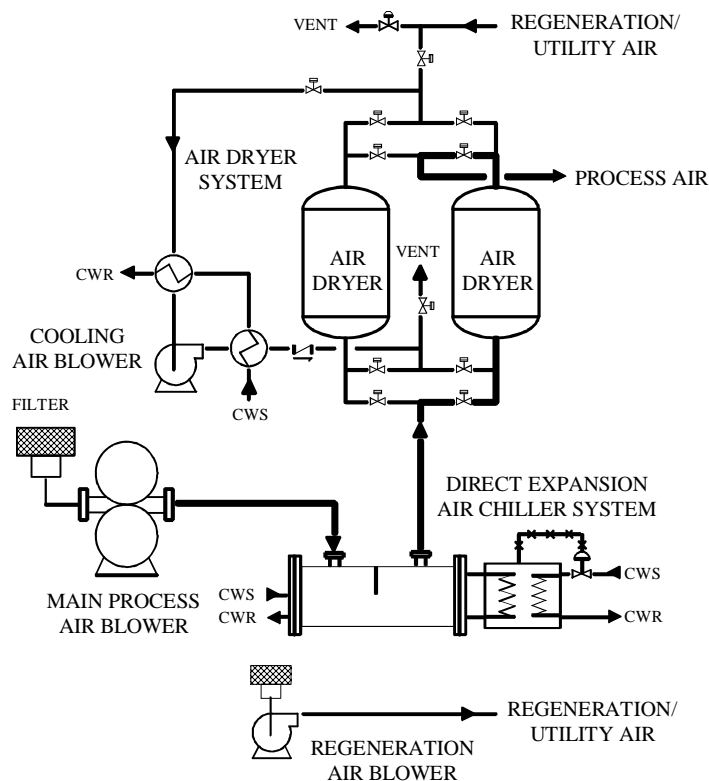
**Figure 19. Continuous Air/SO<sub>3</sub> Sulfonation**



As Figure 20 illustrates, the process air is first compressed to a pressure of approximately 1 kg/cm<sup>2</sup> (15 psig) using either a rotary compressor or a high efficiency centrifugal compressor. In larger sulfonation plants – capacities greater than 4000 kg/hr – the process air capacity should be adjustable without venting between approximately 60 to 100% of full capacity (while maintaining efficiency). This ability conserves electric power if the plant is operated at partial capacity.

A direct expansion air chiller vessel cools the compressed air to a temperature of 7°C (45°F). The chilled air is then dried in dual, automatic pulse-less desiccant-type air dryers to a dew point of -80°C (-112°F). The lack of a pulse in the air stream is vital to product quality. If the air pulses, there will be a momentary interruption in mole ratio which results in a loss of product quality. The result is product with high free oil, dark color and possibly other undesirable by-products. The dual air dryers are equipped with 11 individual bubble tight control valves. The control valves ensure absolutely no interruption of process air when changing dryers and a smooth pressure transition when the dryers switch to regeneration cycle. A cooling air blower supplies cool air to the regenerated (off-line) air dryer to reduce the bed temperature to an acceptable level prior to bringing the regenerated air dryer back on-line. This is important – if the dryer bed is too hot, the process air dew point will be higher than desirable due to the increased equilibrium concentration of water in the hot air exiting the dryer.

**Figure 20. Air Supply System**



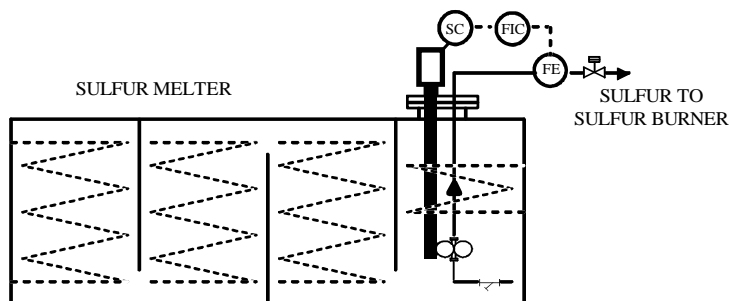
A regeneration/utility air blower supplies cooling air to the double pipe gas coolers used in the gas plant. Hot air (200°C) leaving the low maintenance double pipe coolers

regenerates the off-line air dryer. During the air dryer cooling cycle in smaller plants, the regeneration/utility air vents to the atmosphere or is sent to other processes where the heat in the air can be used. In larger plants (greater than 4000 kg/hr) the heat may be recovered as steam. In this case, the gas plant is modified so that it produces steam instead of hot air and a portion of this steam heats the regeneration air.

In the sulfur supply system shown in Figure 21, bright Frasch or by-product sulfur flows by gravity to one of two gear pumps. Typically dual strainers, pumps, and flow meters are provided minimize down time during maintenance. The sulfur passes through a highly accurate mass flow meter prior to delivery to the sulfur burner. Because the mole ratio is the most important process variable, control of the sulfur flow to the sulfur burning air/SO<sub>3</sub> gas plant is one of the two most important process control functions in the plant. The entire sulfur supply system is steam jacketed because the sulfur has a freezing point of 112.8°C.

Sulfur is normally handled at its viscosity minimum, which is 136°C. A steam and condensate system supplies the necessary tracing circuits for the sulfur supply piping.

**Figure 21. Sulfur Feed System**

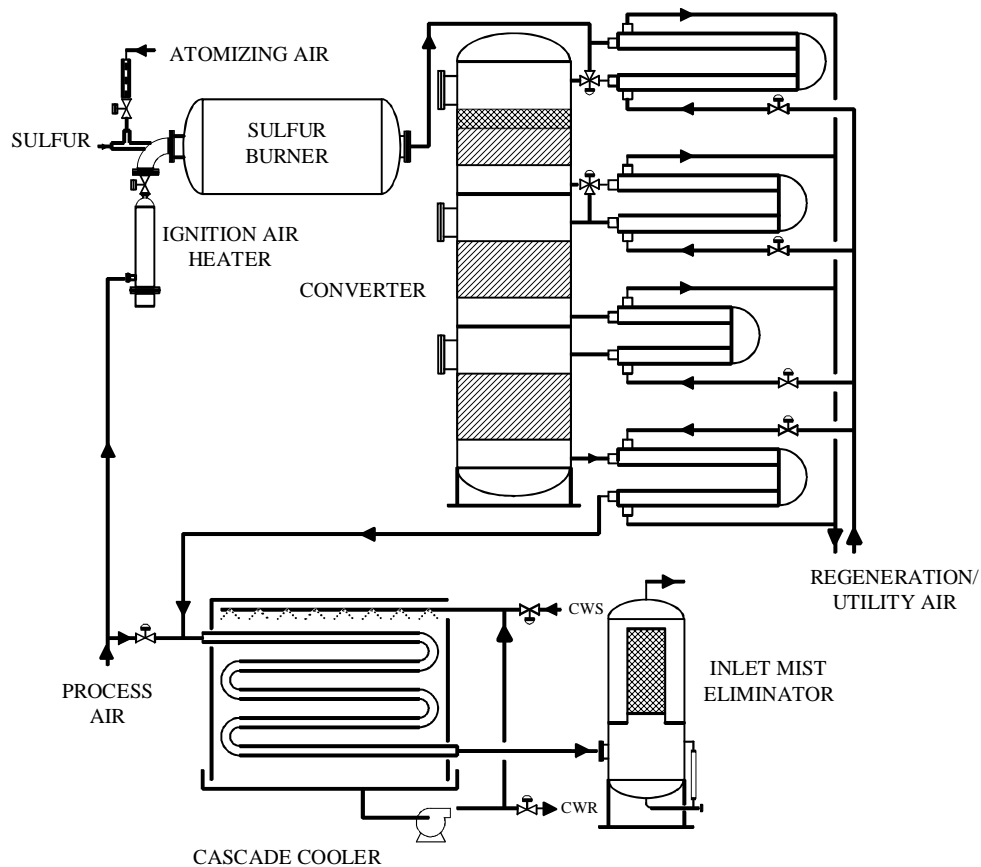


In the SO<sub>3</sub> gas generator, illustrated in Figure 22, the metered sulfur is delivered to the refractory-lined atomizing sulfur burner where combustion with the dry process air generates sulfur dioxide (SO<sub>2</sub>). The atomizing burner ensures instant, constant sulfur burning. The sulfur dioxide gas leaving the burner is cooled to 420°C and delivered to a three-stage vanadium pentoxide catalytic converter, where the gas is filtered and converted to sulfur trioxide (SO<sub>3</sub>). The conversion efficiency of the converter is between 99.0 and 99.5%. Prior to entering the inlet mist eliminator, the sulfur trioxide gas leaving the converter is cooled to nearly ambient temperature in an SO<sub>3</sub> double pipe cooler

followed by an SO<sub>3</sub> water cooled heat exchanger. The inlet mist eliminator removes traces of sulfuric acid or oleum from the cooled SO<sub>3</sub> gas stream. Heat recovered from the second to third pass converter interstage cooler and SO<sub>3</sub> cooler regenerates the air dryers, eliminating the need for an external heat source. Heat recovered from the SO<sub>2</sub> and first to second pass interstage cooler can be used to generate steam in the optional heat recovery system. In state of the art sulfonation plants, computer aided hot gas piping design eliminates troublesome hot gas expansion joints in the gas plant. The enhanced piping design improves significantly plant reliability and eliminates a possible source of inadvertent SO<sub>2</sub> or SO<sub>3</sub> discharge to the environment.

An inline double pipe ignition air heater warms the combustion air stream for sulfur burner preheating and ignition. A gas-fired duct type start-up heater in the regeneration/utility air line preheats the SO<sub>3</sub> and first to second pass interstage cooler. The start-up heater, used during a cold plant start-up, reduces to less than

**Figure 22. SO<sub>3</sub> Gas Generator**





two hours the time required to achieve stable conversion of  $\text{SO}_2$  to  $\text{SO}_3$  so that sulfonation can begin. These features significantly reduce the time required for gas plant start-up and eliminate the use of sulfur as a fuel to heat the gas plant during start-ups. Production of  $\text{SO}_2$ , which must be scrubbed from the exhaust gas prior to discharge to the atmosphere, is minimized, therefore reducing plant operating costs.

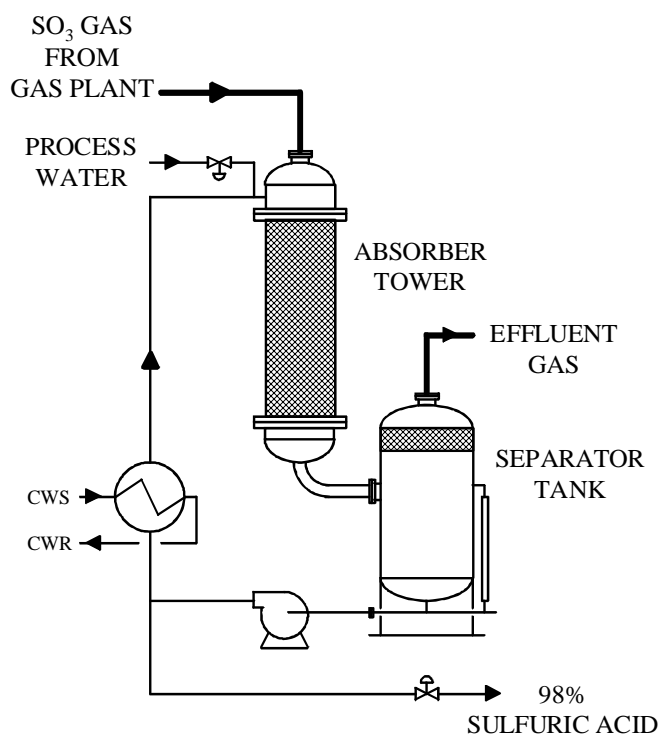
The  $\text{SO}_3$  absorber unit, shown in Figure 23, is capable of treating the total output from the  $\text{SO}_3$  generation system to form 98% sulfuric acid. It is a convenience in plant start-up, shutdown and product changeover. It is also recommended in situations where frequent power failures can interrupt production. With this equipment, the plant can be restarted without forming off-specification product. If this unit is not used, the sulfonation reactor itself must be used to scrub  $\text{SO}_3$  from the process gas during gas plant start-ups. This is an undesirable procedure, however, as the gas plant has not stabilized during the start-up process and the mole ratio of  $\text{SO}_3$  to feedstock is unknown. The practical solution to this problem is to purposely under-sulfonate alkylbenzene during the start-up. The off-specification material made in this start-up procedure can be stored and later blended back into the product. The  $\text{SO}_3$  absorber system is almost a necessity if only alcohol feedstocks are run in the plant, because alcohol sulfuric acids cannot be stored and reused.

$\text{SO}_3$  mixed in air enters the absorber column where it contacts 98% sulfuric acid. The  $\text{SO}_3$  is absorbed into the acid, which separates from the remaining air in the scrubber body. A mesh pad mist eliminator removes entrained acid mist from the air as it exits the vessel. Water is added to control the concentration of the sulfuric acid as it flows through the acid circulation system. An instrument system with dual conductivity sensors holds the acid concentration at 98% by controlling water addition. A heat exchanger in the absorber circulation loop removes heat of dilution.

The sulfonator is the heart of a sulfonation plant. Sulfonic acid forms in the sulfonator when an  $\text{SO}_3$ -in-air mixture is injected into the reactor simultaneously with the desired organic feed under carefully controlled conditions of mole ratio,  $\text{SO}_3$  gas concentration and temperature. Potential organic feedstocks include alkylates, alcohols, ethoxylated alcohols, methyl esters and alpha olefins.



Figure 23. SO<sub>3</sub> Absorber System



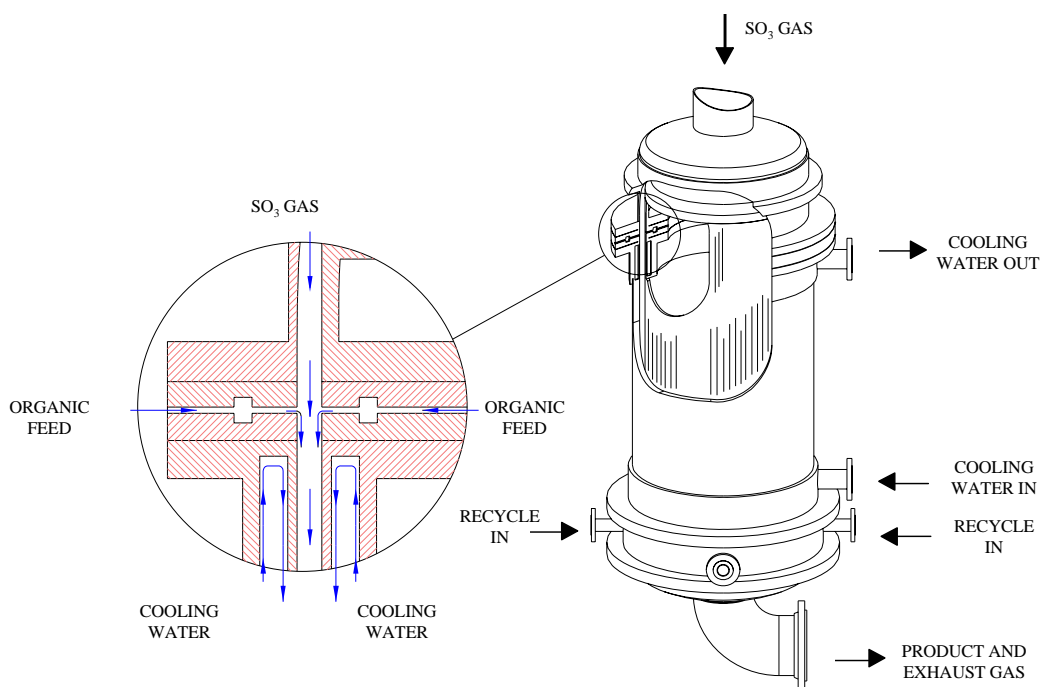
Several types of commercial sulfonators are available. In broad classifications they are film reactors<sup>[6, 7, 8, 9]</sup>, including the Chemithon Annular Falling Film Reactor<sup>[10, 11, 12]</sup>, the Ballestra<sup>[13]</sup>, IIT and Siprec multitube film reactors; the Chemithon dispersed phase or jet reactors<sup>[14, 15, 16]</sup>; and stirred tank or cascade type reactors<sup>[17]</sup>. Film reactors are the most common in detergent processing for consumer products, especially to produce cosmetic quality materials from oleo chemical feedstocks. In a film reactor, the organic feedstock is extruded onto the wall of the reactor (reaction surface) as a continuous film. Organic feed rate to the reactor vessel is measured by a highly accurate mass flow meter and controlled by a variable speed driven gear pump. The proper organic feed rate is based on the preset sulfur-to-organic mole ratio. The SO<sub>3</sub>, diluted with very dry air, flows over the film of organic material. The SO<sub>3</sub> diffuses into the organic film and reacts to form a sulfonic acid. In almost all commercial reactors both the organic and SO<sub>3</sub> flow concurrently from the top of the reactor to the bottom. The heat of reaction is removed by cooling water which flows through cooling jackets underneath the reaction surface of the reactor.

Figure 24 shows a Chemithon Annular Film Reactor. This patented reactor<sup>[10, 11, 12]</sup> is unique in many ways. It employs interchangeable, factory calibrated organic metering flanges. These flanges ensure that the flow of organic to any two points on the reaction surface is equal, within  $\pm 1\%$ . When combined with the geometric design of the reactor that similarly controls the flow of  $\text{SO}_3$  to the reaction surfaces, these features ensure that mole ratio control is maintained on a micro scale throughout the sulfonator. Cooling jackets on the reactor remove most of the heat of reaction. Additionally, the patented recycle system allows the reactor to overcome the increase in viscosity of the sulfonic acid as its level of sulfonation increases. The product exiting the reactor is instantly quench cooled by removing the acid, pumping it through a heat exchanger to cool, then returning it to the bottom of the reactor. This cooling process reduces the time that the sulfonic acid is held at an elevated temperature and results in better product quality. A side benefit is that the reactor is more compact – less than two meters in height – and therefore considerably less expensive to install.

Figure 25 shows this reactor installed in a typical sulfonator. Upon exiting the reactor, the spent gas is separated from the sulfonic acid recycle stream in the liquid separator and cyclone vessels. Sulfonic acid product discharges from the recycle stream at a controlled rate, maintaining continuity of the quantity of material in the reactor system. The acid product from the reactor can then be fed directly to the digestion and hydration system (or optional degasser system) where reaction with absorbed  $\text{SO}_3$  is completed. Hydration water is injected and mixed with the sulfonic acid, leaving the digesters to remove anhydrides.

Figure 26 shows a typical multi-tube sulfonation reactor<sup>[9, 13, 18]</sup>. The multi-tube reactor is the other commonly employed film sulfonator design. In this reactor the organic feed is distributed among a number of parallel reaction tubes, 25 mm in diameter, 7 meters long. The tubes are arranged like the tube bundle in a vertical shell and tube heat exchanger. The organic and  $\text{SO}_3$  gas flow concurrently down the reactor tube, react and exit the bottom of the reactor into a separator vessel. The heat of reaction is removed by cooling water which flows through the reactor jackets. The approximate residence time of the acid from the top of the reactor through the separator and cyclone and to the neutralizer is two to three minutes.

**Figure 24. Chemithon Annular Falling Film Reactor**

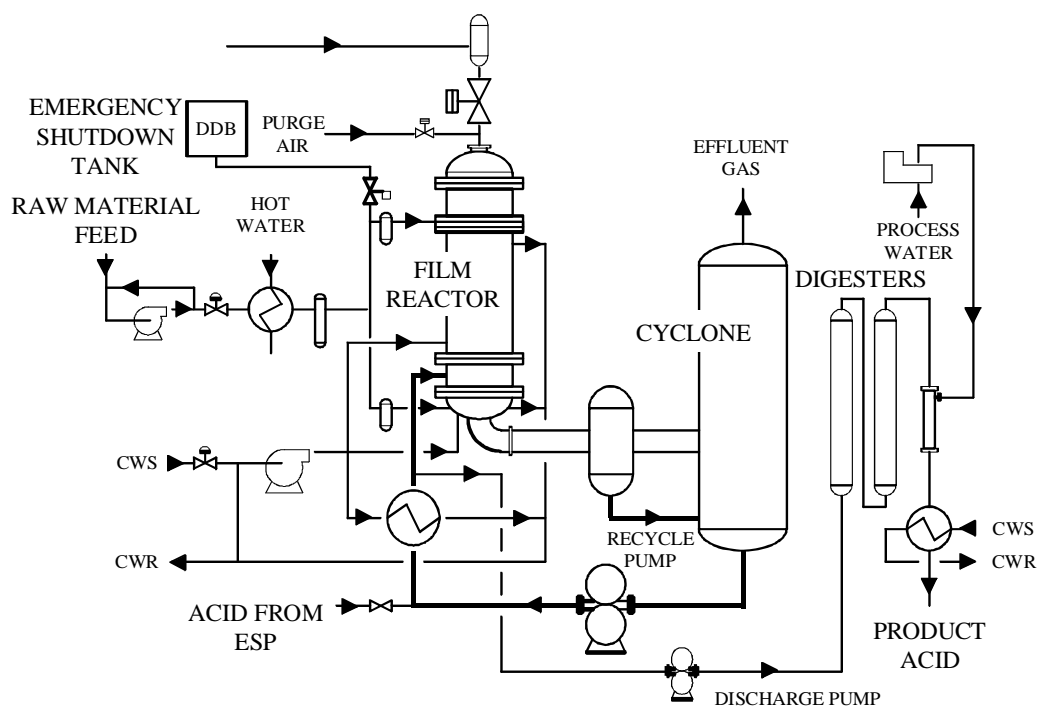


Stepan Company<sup>[7]</sup> patented a multi-tube reactor in 1965. They currently operate a large number of these reactors worldwide. Similar reactor designs are manufactured by other firms<sup>[19, 20]</sup>.

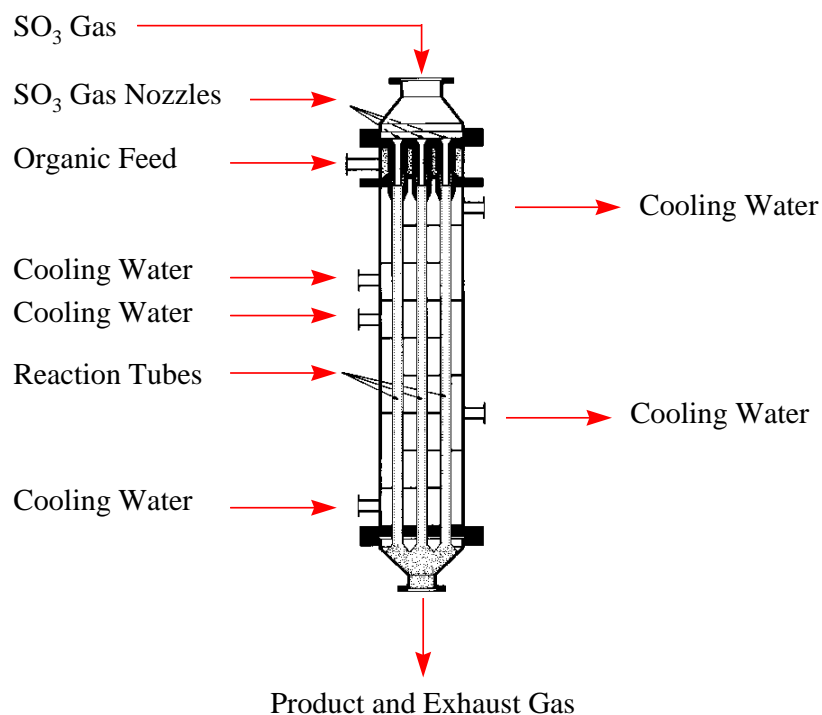
A continuous neutralizer system is illustrated in Figure 27. The neutralizer combines sulfonic acid or organo-sulfuric acid with a neutralizing agent, additives, and diluent (water), in a dominant bath neutralization. The result is a solution of neutral active matter (slurry or paste) of the desired composition and pH. Caustic soda, usually 50 wt% NaOH, is the most common neutralizing agent. However, caustic potash, aqueous ammonia, triethanolamine, and other agents are compatible with the neutralizer. A recycle loop circulates neutral slurry through a heat exchanger to remove heat of neutralization, mixing and pumping. Individual metering and/or gear pumps feed sulfonic acid, neutralizing agent, dilution water, buffer solution and any additives into the loop to mix through a high shear mixer. A positive displacement pump circulates paste

through the process heat exchanger and a large portion of this stream recycles back to the mixer. A pressure control valve allows product to leave the recycle system as feed enters. A pH sensor is placed in the recycle line near the inlet to the mixer. The in-line pH sensor measures an accurate pH on dilute slurries, and produces a single-valued output signal that is proportional to pH on concentrated pastes. The signal from the sensor feeds to the pH control system in either case, and controls the flow of the neutralizing agent into the process. Use of a buffer promotes stability in the pH control loop. Cooling water is also recirculated and automatically adjusted to maintain a desired temperature at the process heat exchanger inlet. Therefore, higher melting point products can be processed without plugging the heat exchanger during start-up.

**Figure 25. Sulfonation System**

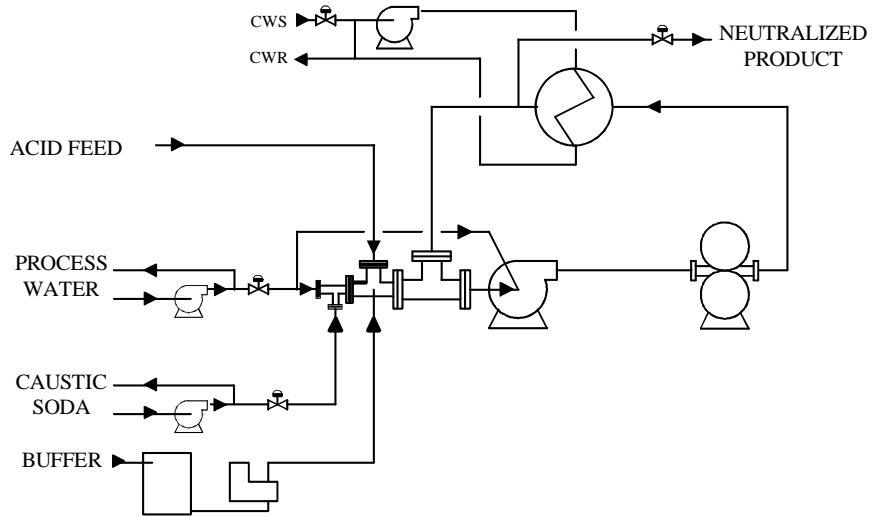


**Figure 26. Ballestra Multi-Tube Film Sulfonator**

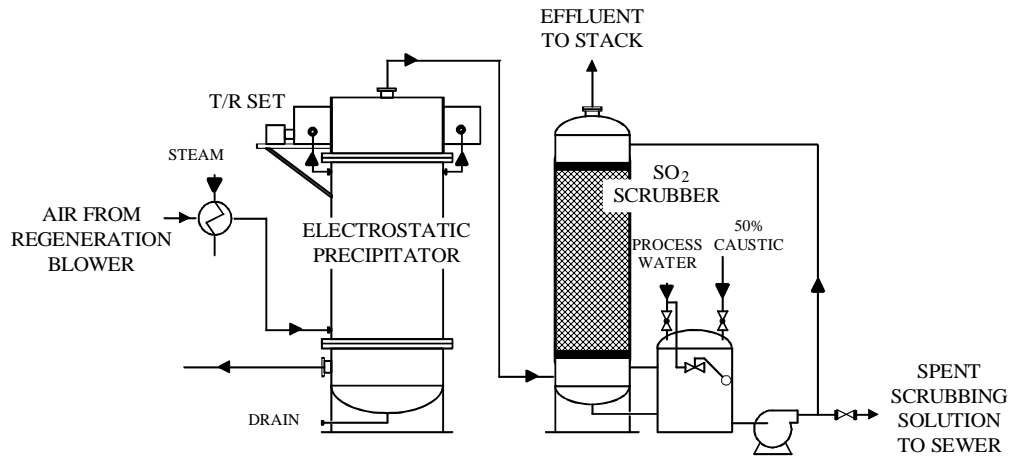


Effluent process gases leaving the sulfonation system or  $\text{SO}_3$  absorber are virtually free of residual  $\text{SO}_3$ , but contain any unconverted  $\text{SO}_2$  gas and entrained particulate anionic materials (acidic mists of sulfonic and sulfuric acids). This gas stream is not suitable for direct discharge to atmosphere. The recommended clean-up system, shown in Figure 28, employs an electrostatic precipitator designed to collect particulate mists and a packed tower scrubber to absorb  $\text{SO}_2$  gas in a dilute caustic. Final effluent gases cleaned to contain less than 5 ppm<sub>v</sub>  $\text{SO}_2$  and less than 10 mg/m<sup>3</sup> combined sulfate mist and neutralized organic mist are suitable for discharge to the atmosphere.

**Figure 27. Neutralizer System**



**Figure 28. Effluent Gas Treatment System**





## ***Sulfonation Plant Control***

A typical sulfonation plant control system consists of two components that are integrated into a single system: A main instrument control panel (ICP) and a motor control center (MCC). When properly designed and installed, this system not only allows operation of the sulfonation plant but also improves the operators' understanding of the plant's operation through graphic interfaces. Better control results in improved product consistency and quality.

The ICP integrates the loop control, logic control, data acquisition, and operator interface into a single system. The functions include: analog control or PID control loops; discrete control, e.g., to automatically sequence valves in the air dryers, and when diverting gas from the sulfonator to the SO<sub>3</sub> absorber; interlocks to reduce operator errors that could result in damage to the equipment or environmental releases; alarm monitoring; and recipes that automatically enter variables used to calculate set points for organic feed and the neutralizer raw materials.

The hardware can be as simple as individual electronic controllers or as complicated as integrated, plant-wide distributed control systems. Naturally, more complex and expensive control systems allow more control functions and permit data logging. They also reduce the dependence on operator knowledge to produce top quality products.

As a cost effective option which allows maximum control at minimum cost, many sulfonation plants employ a PLC-based control system in which the operator interaction is accomplished by at least two, redundant PC-based workstations. These workstations connect directly to the controllers and supply the operator with information necessary to operate the plant. Normally a graphic display package is included in the control system software. It shows graphic representations resembling a Process & Instrumentation Diagram, which displays the main operating variables and indicates which motors are operating. Typical displays include: sulfur metering system; air dryer system; SO<sub>3</sub> gas generator system; sulfonator system; neutralizer system; and effluent gas treatment system. The system is also capable of trending selected variables, logging alarms and collecting data for historical logs.

The motor control center (MCC) includes a main power disconnect, a lighting transformer, motor starters, variable frequency speed controllers, and disconnects as required for the equipment.



## ***Future Trends***

The detergent market is rapidly changing as a result of three interrelated drivers. The first is the "green" movement in which consumers are demanding environmentally friendly products and packaging. The second is the move toward compact detergents which eliminate large bulk fillers from detergent formulations. The third is a desire on the part of consumers for "natural" products which are perceived as purer and less harmful to the environment. All of these forces are moving detergent producers to modify their processes and their choice of feedstocks.

The rapid increase in the market share of compact detergents indicates that large quantities of sulfates are no longer acceptable in detergent actives. This trend, in conjunction with the increased cost of spent sulfuric acid disposal, has helped eliminate oleum sulfonation as a viable technology for detergent manufacture. This change has been accentuated by a move toward use of natural feedstocks such as oleo chemical based alcohols and methyl esters. Because the feedstocks are made from renewable resources, they are perceived by consumers to be somehow cleaner and purer than petrochemical-based raw materials. The net result is that oleum sulfonation and sulfation technology is increasingly being replaced by air/SO<sub>3</sub> technology.

The purity issue is being hastened by consumers' interest in products containing low levels of impurities or by-products. Colorless products carry the perception of purity and are therefore currently favored by consumers. Again the movement is toward very light colored materials which are typically air/SO<sub>3</sub> sulfated alcohols and alcohol ether sulfates. Manufacturers of other feedstocks such as linear alkylbenzene have responded to this challenge by introducing new grades of feedstocks. These new feedstocks are specially prepared so that color formation on sulfonation via air/SO<sub>3</sub> is minimized. Some of these feedstocks will produce sulfonates which rival alcohols for lightness of color.

Another by-product which has received wide spread attention in Europe is 1,4-dioxane. This by-product is formed during sulfation of ethoxylated alcohols. The mechanism for its formation has been studied extensively and most sulfonation equipment suppliers can guarantee 1,4-dioxane levels of less than 30 ppm on a 100% active basis in ether sulfates without stripping. The most obvious strategy in dealing with 1,4 dioxane is to avoid forming it. However, if you have an existing plant or if undetectable levels are required, equipment is available to strip the neutral product to remove any traces of 1,4-dioxane. This technology allows existing equipment to be run at full capacity while permitting manufacturers to produce essentially 1,4-dioxane-free product.

The attention focused on compact detergents has created an interest in very high active sulfonates and sulfates. If active levels are sufficiently high, these products can be



directly agglomerated to form compact laundry detergents without spray drying. This ability is a major advantage because it allows manufacture of a finished laundry formulation in low cost equipment – without the energy and environmental penalties of spray drying. Chemithon has developed high active neutralization technology capable of producing 70–80% active neutralized sulfonates or sulfates from any of the normally used detergent feedstocks.

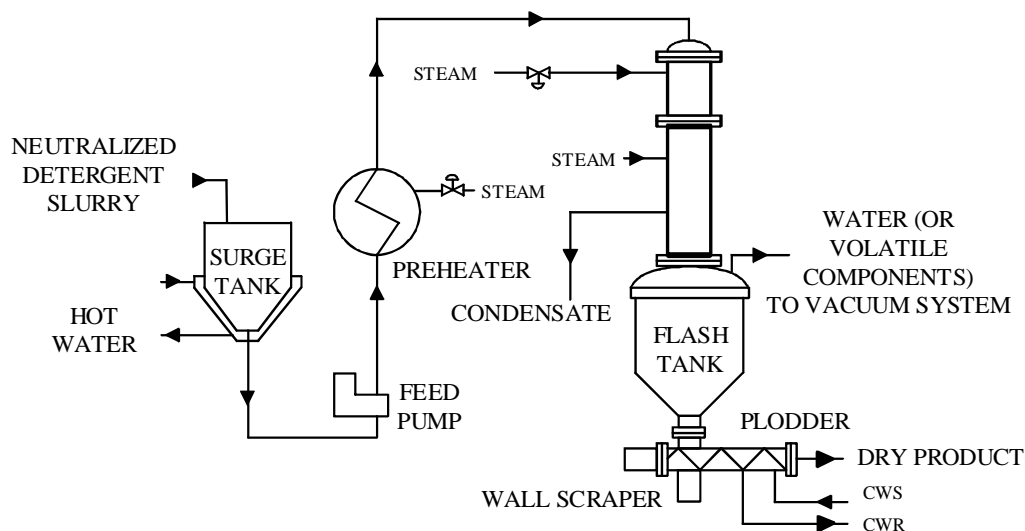
These high active pastes can then be dried to very low moisture levels ( $\leq 5\%$ ) in either a wiped film evaporator or in the Chemithon Turbo Tube™ dryer. This equipment removes moisture from the detergent paste to produce a detergent noodle, needle, pellet or powder which can be agglomerated into the finished detergent formulation or shipped to the formulator for further processing.

### ***Additional Equipment***

The Chemithon Turbo Tube™ dryer (patent pending), shown in Figure 29, is a heated, vacuum flash device in which the volatile components of a surfactant slurry are removed in a non-dusting manner. The process is carried out under carefully controlled conditions of temperature and pressure to ensure that product quality of sensitive surfactants is not compromised during the removal process. Because of the low production costs of this new technology, the surfactant manufacturer can supply a low cost, inexpensive dried detergent active to the formulator. Transportation costs are significantly reduced as well, because water and other possible diluents are removed prior to shipping. The formulator can use this source of active to customize the final formulation for his particular market using inexpensive agglomeration equipment.

Production of sodium alpha sulfo methyl ester (SASME) is the final advance in sulfonation technology discussed in this chapter. Because of the vast quantities of methyl ester produced world wide (estimated to exceed 540,000 tons in 1995<sup>[21]</sup>), there is widespread interest in using this raw material for detergent production. The Chemithon Corporation has developed a new bleaching process for production of low disalt, light colored SASME. Chemithon has applied for patents to cover this new process. The process, shown in Figure 30, combines hydrogen peroxide, methanol and digested methyl ester sulfonic acid. The hydrogen peroxide bleaches the methyl ester, while the methanol is essential to prevent hydrolysis of the methyl ester to a disalt and methanol. Reducing disalt is important, as disalt decreases solubility and detergency of SASME in hard water and shortens shelf life of detergent formulations. Even if no methanol is added to the process, methanol forms from degradation of the methyl ester under the acidic

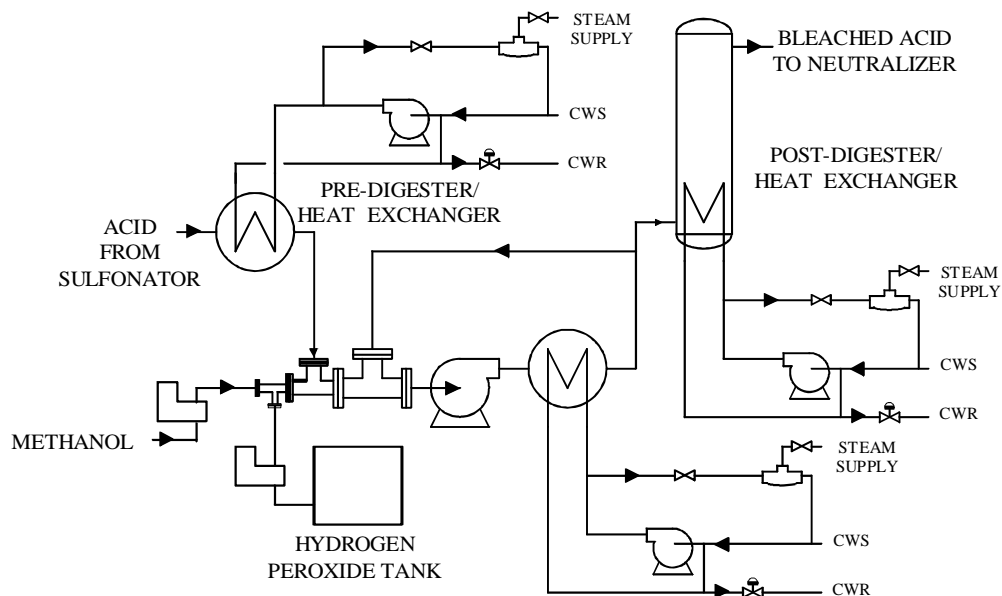
**Figure 29. Turbo Tube™ Drying System**



bleach conditions. The use of the methanol prevents this and makes it possible to bleach the methyl ester to a color of less than 50 Klett in a single step, without using sodium hypochlorite. It simultaneously keeps the disalt levels below 5% on an active basis.

The SASME product leaving the neutralizer contains approximately 65 to 70% solids and 10 to 20% methanol. Methanol and water are removed from this material in the Turbo Tube™ Dryer, separated and recycled back to the process. The dried SASME is pumped from the dryer and cooled. The "needle" making apparatus forms the material into small uniform particles ("needles") containing less than 0.5% methanol and less than 5.0% water. This system is also applicable to processing other detergent actives such as alcohol sulfates or linear alkylbenzene sulfonates into dry detergent needles.

**Figure 30. ASME Esterification and Bleaching System**



The past 50 years have seen the rise of synthetic, anionic detergents as a major item of commerce. The processes used to manufacture these detergents continue to improve as the consumer market drives producers to offer cleaning products with lower cost and improved performance. This trend will continue as consumers broaden their definition of performance to include environmental and purity concerns.



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