Summary

Soap manufacture from fatty acids is a well established process with some advantages over continuous saponification of neutral fats. These include:

1) Ability to use cheaper fats.
2) Easier glycerol recovery.
3) Better control over by-products.
4) Versatility—fatty acids can be used to make other derivatives than soaps.

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Continuous Sulfonation Techniques

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THE SULFONATION of alkyl benzene and the sulfation of fatty alcohol have been under continuous study not only by the detergent manufacturers, but also by the suppliers of detergent manufacturing equipment and of detergent raw materials.

When detergents were first introduced to the market they were generally in powder form and the active ingredients employed could contain large amounts of sodium sulfate without presenting any undue problems. However, with the advent of the liquid products, active ingredients containing little inorganic salt were essential—and it is this fact which has stimulated, to a major extent, the development work on sulfonating with SO_3 rather than with oleum.

I think that it will be worth a few minutes of our time to follow briefly the development of the sulfonation process so that we might better appreciate the problems that had to be overcome to arrive at the present stage—that is, sulfonation using gaseous SO_3 produced directly from the burning of sulfur.

Throughout this discussion keep several points in mind:

1) Product quality is the key to the acceptability of a process, and for alkyl benzene the specifications are: 98% completion of reaction and a white paste upon neutralization with the alkali.
2) The color of the neutralized paste is good or bad depending upon the ability of the process to remove the heat of reaction instantaneously.
3) The heat of reaction for the sulfonation increases with increasing oleum strengths—and is a maximum when SO_3 is used.

Thus it is easy to understand that the first production units were batch plants and the sulfonating agent was 10–20% oleum. In these plants the alkyl benzene was weighed and placed in a tank; then the oleum was slowly added until the quantity required by the formula was also placed into the tank. With the two reactants now intimately mixed, they were now permitted to digest for 30–45 min. After the digestion period the neutralization of this acid mix was carried out.

Continuing engineering development work—to more efficiently remove the heat of reaction at the point of contact of the oleum with the alkyl benzene—soon permitted the use of 25% oleum.

The next stage in the development of the sulfonation process was that of continuous processing rather than batch. Here the only advantages were possibly lower plant costs and lower operating costs, since there was not any improvement in product quality.

Later came High Active Ingredient (AI) which allowed the separation of the major portion of the sulfuric acid present in the acid mix prior to neutralization. Product with an active content of 87–88% on a dry basis can be produced by such a process.

But many liquid formulas demanded still higher active contents. The advent of stabilized liquid SO_3 made it possible to economically prepare a product with 96–97% AI on a dry basis. The suppliers of this stabilized liquid SO_3 developed batch processes which included the vaporization of the liquid SO_3, diluting this with dried air to approximately 10% by volume, and contacting this gaseous stream with alkyl benzene previously weighed and placed in the reactor tank. Although the use of liquid SO_3 has economic advantages over the use of oleum, it was the inability of this process to match the product quality produced on the oleum plants that prevented it from being readily accepted by the major detergent manufacturers. It should be mentioned that there is one manufacturer who claims to have a continuous process using vaporized SO_3 but there are no details available on this.

There is another batch process operating today which uses the technique of reacting liquid SO_3 with alkyl benzene in the presence of liquid SO_2—and conducting this reaction at very low temperatures. The product produced by this process is excellent. Mr. Morrisroe pioneered the commercial development of this process.

Now we come to the latest stage of development for the sulfonation reaction—and this is the burning of sulfur to produce the required SO_3 and coupling this directly to the sulfonation reactors for continuous operation.

This combination of sulfur burning and sulfonation has economic advantages and has been worked out to a high degree of precision by the Ing. Mario Ballestra Co. There are others who have followed this type of processing and we will attempt to show the basic differences between various processes. Very few details are available concerning other processes. Therefore our attempt to compare other operations to the Ballestra process will perforce be somewhat sketchy.

Chemically all three processes are identical. Starting with sulfur, burning to SO_2, converting to SO_3, and feeding this stream continuously and directly to the sulfonator for reaction with the organic material to be sulfonated or sulfated. Let me point out that vaporized SO_3 could also be used in these plants but the economics generally favor the use of sulfur.

The processes generally differ in their approach to the removal of the heat of reaction—at the moment of contact of the SO_3 and the alkyl benzene. One uses the "dominant bath" idea combined with having the reaction occur on the heat exchange coils. In the "dominant bath" technique the recycling mass of sulfonic acid is used as the medium to quickly absorb the heat of reaction of the freshly added reactants. Generally significant residence time is required here, and this can be an advantage as will be pointed out later.

A second process uses a mechanically agitated film with heat transfer taking place through the external walls of the reactor as well as through heat exchangers. This reactor has very low holding time.

The third process is a true film reactor where the liquid is maintained as a thin film moving along a tube and the SO_3 is brought into contact with this film at the surface. The heat is removed immediately through the tube wall. This reactor too has very low holding time.

Description of the Ballestra Sulfurex Process

Since I know this process intimately, I would like to present a detailed description of this sulfur burning-SO_3 sulfonation plant which over the past four years has been in operation and is being used widely.

Air Handling and Purification

The air required for the burning of sulfur and for the conversion to SO_3 is filtered and passed through one of a pair of Silica Gel driers where all the moisture is removed. The Silica Gel driers are placed in parallel so that while one is in operation drying the incoming air, the other is being regenerated. From the Silica Gel driers the air then passes into a blower from which it is delivered steadily and constantly to the sulfur burner.

Sulfur Feeding and Burning

The handling of sulfur is quite simple and free from hazards when it is compared to the problems and danger connected with the handling of oleum and liquid SO_3. If solid sulfur is being used, it is taken from storage by a screw conveyor and fed to the sulfer melter. The design of this melter is such that the impurities can be easily separated leaving pure sulfur for feed to the sulfur burner.

From the melter the liquid sulfur passes to a proportioning pump which very precisely meters the sulfur. This sulfur pump is steam jacketed to maintain the temperature of the sulfur above its melting point, and also is capable of being adjusted during operation if it is desired to vary the plant capacity.

This sulfur metering pump delivers the molten sulfur to the sulfur burner where it is contacted, counter-currently, with the required volume of air to produce SO_2. The SO_2 content of the gases exiting from the burner is 7% by volume. The temperature at the outlet of the burner is about 700C and these gases must be cooled—by means of a heat ex-

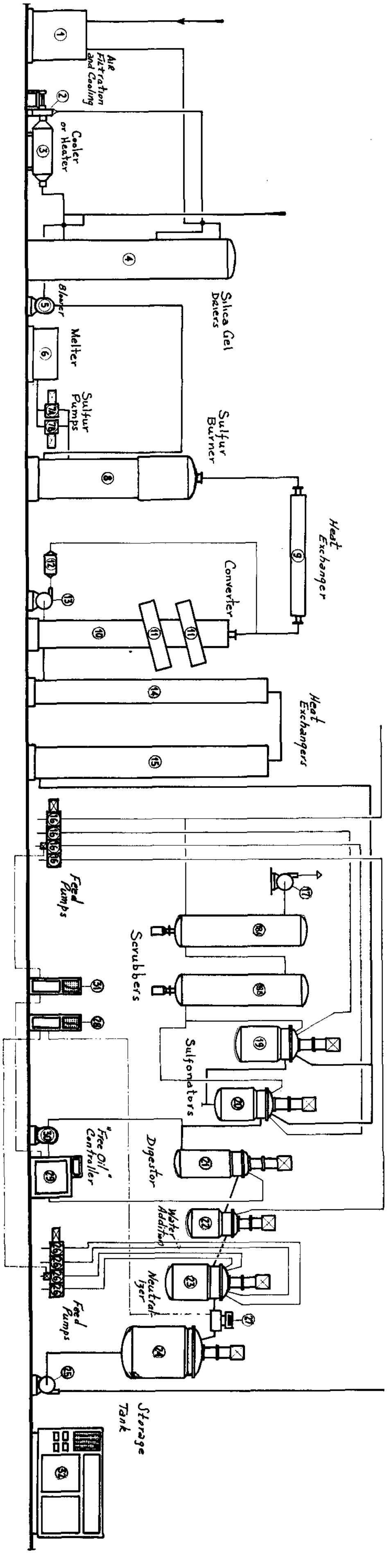

FIG. 1. Flow diagram of Ballestra Sulfurex Process.

changer—to approximately 420C, which is the optimum temperature for maximum conversion of SO_2–SO_3 in the conversion tower.

The conversion tower is designed with four beds of vanadium pentoxide catalyst to insure complete conversion within the tower, but experience has shown that three passes are sufficient to give the full conversion of SO_2–SO_3. The conversion temperatures are approximately:

1st pass inlet	420C
1st pass outlet	560C
2nd pass inlet	435C
2nd pass outlet	490C
3rd pass outlet	435C
Tower outlet	450C

Because of the heat release as the SO_2 is converted to SO_3 heat exchangers are located between the first and second pass and also between the second and third pass to bring the temperature of the gases back down to the 420–440C optimum.

Now the temperature of the gases leaving the conversion tower, containing approximately 8% SO_3, must be cooled down to 70C before entering the sulfonators. For this, two heat exchangers in series are used.

The heat removed in the various heat exchangers is used to regenerate the Silica Gel driers, and therefore there are no costs involved in drying all the air that is used in this process.

Sulfonation

After being cooled to 70C, the SO_3 gas stream passes into the sulfonators. The sulfonators consist of two or more reactors—different in number and size depending on the capacity of the plant. The SO_3 gas stream enters the reactors in parallel with the major portion entering the first reactor and the minimum portion entering the last reactor. This proportioning of the SO_3 gas into the various reactors is done automatically and requires no attention from the operator.

The alkyl benzene (or any other material to be sulfonated or sulfated) essentially passes through the reactors in series, but because of the "Free Oil" controller, a small amount is proportioned into the last reactor since it is this amount which is varied more or less depending on the completion of reaction.

Special high speed turbines disperse the SO_3 gas and the alkyl benzene with a high degree of efficiency which prevents any local overheating of the reactants. Cooling coils and baffles are precisely placed within the reactor to immediately remove the high heat that is released during the reaction.

The temperatures normally used for various raw materials are:

a) for the usual types of alkyl benzene (branched or straight-chained)
   Sulfonators: 50C
   Digestion: 55C
   Neutralization: 45C
b) for lauryl alcohol:
   Sulfonators: 35C
   Neutralization: 45C
c) for tallow alcohol:
   Sulfonators: 55C
   Neutralization: 50C
d) for C_{14}–C_{18} Alfol (Continental Oil Co.):
   Sulfonators: 50C
   Neutralization: 45C

After the sulfonators the main stream of sulfonic acid passes on to the digestion vessel where sufficient holding time is provided to permit the reaction to go to completion. A side portion of this stream is directed to a patented device which automatically analyzes the sulfonic acid and determines its "Free Oil" content. If the Free Oil is increasing, this control unit automatically cuts down on the quantity of alkyl benzene being fed to the last reactor, and conversely, if the Free Oil is going too low, then the unit automatically increases the flow of alkyl benzene to the last reactor.

The gases from the reactors are essentially free of SO_3. However, the plant is equipped with two scrubbing towers—one for removing any SO_3 gas that may be in the exit stream, and a second, in series, for scrubbing out the SO_2, so that the exhaust gas is free of any of these undesirable components as it passes to the atmosphere.

After the digestion vessel, the sulfonic acid stream can be passed into another small reactor where water can be added if desired. This unit is to take care of any anhydride formation that may occur.

Of course, none of the aging vessels are used during the sulfation of the fatty alcohols and can be by-passed. Because of the combination of reactors it is very easy to perform co-sulfonation-sulfation reactions and produce a high quality product.

The sulfonic acid then passes on to the neutralizer where caustic and water are continuously added to give a white paste containing the desired percentage of Active Ingredient. An automatic pH control unit controls the addition of caustic by sending a signal to the controller which varies the stroke of the proportioning pump of the neutralizing agent by means of a servomoter.

The neutralized paste overflows into a storage tank where it is continuously homogenized. From here it is pumped on to whatever further processing is to be done, such as spray drying, liquid production, etc.

It is important to note that from the sulfonators on there are no transfer pumps required. The reactants and acid flow from vessel to vessel by gravity. Operation and control of this plant is extremely precise and yet simple. One operator runs the entire plant—sulfur burning, conversion, and sulfonation.

Finished Product Obtained

With alkyl benzene the neutralized paste contains, on the average:

97.5% Active on a dry basis
1.5% Sodium Sulfate in a dry basis
1.0% Free Oil on a dry basis (extraction method)
Color: White

Other Types of Reactors

There are other types of reactors which differ from the one just described in detail, mainly in the techniques used in removing the heat of reaction. One entails the use of a falling film with the gas injected into the center of the tube. The reaction occurs on the surface and the heat of reaction is removed through the walls of the tube. The other uses a mechanically agitated film with the heat of reaction removed through the stationary wall of the reactor and through the use of an after heat exchanger.

Both these devices have very short holding times and require excellent control over the metering of the reactants.