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SEPARATION OF SULFONIC ACID FROM EXCESS
SULFONATING AGENT

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This invention relates to the separation of sulfonic acid from excess sulfonating agent and, more particularly, to said separation in the absence of extraneous gas or at a vapor pressure less than normal atmospheric pressure.

A number of processes have been employed for reacting an alkyl benzene having ten to eighteen carbon atoms in the side chain with a sulfonating agent to produce an alkyl benzene sulfonic acid, and also a number of processes have been employed to separate the alkyl benzene sulfonic acid from the excess sulfonating agent. A typical batch-type reaction process may be carried out in a 2,500 gallon glass-lined vessel having a mixer for agitating the reaction mixture. Additional mixing is provided by an external circulation system which discharges into the top of the sulfonator through a distributor head. A heat exchanger of about one thousand square feet is employed in the circulating system to remove the heat of sulfonation. Stainless steel (type 316) is satisfactory for the circulating system and may be used for the reactor if desired. The sulfonation cycle starts with the charging of fourteen hundred gallons of an alkyl benzene to the vessel. Circulation of alkyl benzene is started through the exchanger and sulfuric acid is slowly added to the alkyl benzene at the suction side of the circulating pump. The acid addition rate is controlled so that the reaction temperature does not exceed 85° F.; usually about one and one-half to two hours are required for the acid addition. After seven hundred and forty gallons of twenty-two (22%) percent oleum have been added the mixture is digested at 85° F. for one hour. With these conditions 98-99 percent of the alkyl benzene is converted to alkyl benzene sulfonic acid. A typical analysis of the stock at this stage shows on a percent-by-weight basis: sulfuric acid, 60-61%; sulfuric acid, 38-39%; water, 0.5%; and, residual oil, 0.5%.

A continuous process may be employed for the sulfonation of an alkyl benzene. In this process the equipment consists of a fifty-five gallon sulfonator, a 102 square foot heat exchanger and a 135 gallon digestion vessel. Alkyl benzene is charged continuously to the sulfonator at a rate of 233 pounds per hour. From the sulfonator the alkyl benzene acid mix is recirculated through a centrifugal pump and the heat exchanger. Twenty-two (22%) percent oleum is charged to the pump inlet at a rate of 252 pounds per hour. The sulfonation mix is continuously transferred to the digestion vessel from where it is pumped either to a concentrator or directly to a neutralizer. Sulfonation and digestion temperatures are maintained at 85° F. A 97-98% conversion of the alkyl benzene is realized by this method.

Turning now to the process for separating the alkyl benzene sulfonic acid from the excess sulfonating agent, it has been found that the excess sulfonating agent should be diluted with water to lower the concentration to a value of approximately eighty (80%) percent sulfuric acid so as to obtain a substantially complete separation of the sulfuric acid from the sulfonation mix. This is a result of the mutual insolubility of the sulfonic and sulfuric acids. This dilution step requires a thorough mixing of the diluted sulfonated mix in order to remove the localized gel structure formed between the sulfonic acid and the water. The temperature during dilution is controlled to a value in the range of 135-145° F. maximum so as to

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minimize the color degradation of the alkyl benzene sulfonic acid. If the temperature increases to above approximately 145° F., even with the decrease in the concentration of the sulfuric acid, there is further reaction between the alkyl benzene sulfonic acid and the sulfuric acid to degrade the color of the sulfonic acid. If the acid is diluted below approximately eighty (80%) percent sulfuric acid the product obtained does not have any higher active content of sulfonic acid but the settling time required to separate the sulfonic acid and the sulfuric acid is somewhat reduced. However, the chief disadvantages of greater dilution are that corrosion of stainless steel equipment (sulfonator and heat exchangers) is greatly increased and the color quality of the product is poorer. For example, laboratory tests indicate that the corrosive rate of sixty (60%) percent sulfuric acid dilution is up to approximately one hundred times that of eighty (80%) percent sulfuric acid dilution.

Turning now to the specific separation of the sulfonic acid from the excess sulfonating agent for the batch process employing a 2,300 gallon batch of alkyl benzene, the excess sulfuric acid is diluted to a concentration of approximately eighty (80%) percent strength and the temperature range is maintained in the range of approximately 130-135° F. For this 2,300 gallon mixture a four-hour settling time is required to yield a product comprising approximately eighty-five (85%) percent sulfonic acid and fifteen (15%) percent extraneous material.

A continuous process for separating sulfonic acid from excess sulfonating agent involves the use of a centrifuge. More particularly, the sulfonating batch is diluted with water to form a mixture comprising sulfonic acid and eighty (80%) percent sulfuric acid. The temperature range of the mixture is maintained within the range of approximately 130-135° F. This mixture is centrifuged to separate the sulfonic acid from the sulfuric acid. An advantage of this process over the batch process of settling is a higher quality product as the time of contact between the sulfonic acid product and the excess sulfonating agent, i.e., sulfuric acid, is much less than in the batch process and also the temperature of separation is less than approximately 130-135° F.

Our invention relates to a method for the rapid separation of sulfonic acid from excess sulfonating agent and which method encompasses the carrying out of the reaction under conditions conducive to the rapid separation of a sulfonic acid from the excess sulfonating agent. Briefly, this process comprises the carrying out of the reaction and the separation of the excess sulfonating agent from the sulfonic acid under conditions free from extraneous gas, and with a large quantity of excess sulfonating agent.

Accordingly, it is an object of our invention to provide a process for the quick separation of sulfonic acid from the excess sulfonating agent.

Another object is to provide a process directed to clean separation of excess sulfonating agent from the sulfonic acid.

A further object is the provision of a process for separating sulfonic acid from excess sulfonating agent and which process can be carried out at lower temperatures than previously known and employed processes.

A further and important object is the provision of a process which leads to a higher quality product as there is less degradation of the sulfonic acid product because of the fast separation of the product and excess sulfonating agent.

A still further object is the provision of an inexpensive process for separating sulfonic acid from the sulfonating agent.

Another object is the provision of a process which can be carried out in inexpensive equipment.

A still further and important object is the provision of a process for the separation of sulfonic acid from excess sulfonating agent and which process requires a small amount of equipment and a minimum of housing for this equipment.

These and further objects and advantages of the invention will become more apparent from the following specification, specific disclosure of the same, and the claims.

Turning now to a specific disclosure of one manner of carrying out this process, it is seen that important factors in the separation of the alkyl benzene sulfonic acid product from the excess sulfonating agent, are the concentration of the sulfonating agent in the mixture, the temperature, the degree of agitation of the mixture, the quantity of excess sulfonating agent, and the amount of entrained gas in the mixture.

More particularly, in order to rapidly separate the sulfonic acid from the excess sulfonating agent, it is necessary to form an emulsion comprising as the continuous phase the excess sulfonating agent and as the discontinuous phase the sulfonic acid product dispersed therein. This emulsion is of a lower viscosity than the emulsion comprising as the continuous phase the sulfonic acid product and as the discontinuous phase the excess sulfonating agent dispersed therein. Because of this lower viscosity the sulfonic acid and the excess sulfonating agent rapidly separate from each other. One of the main requirements to realize this lower viscosity emulsion is the maintenance of a minimum volume of the sulfuric acid layer. For example, in order to maintain an emulsion having the excess sulfonating agent as the continuous phase, it is necessary to have about thirty-five (35%) percent by volume of the excess sulfonating agent phase. It has been found that if the acid is in the range of approximately 75-86% strength sulfuric acid a rapid separation of the sulfonating agent and sulfonic acid takes place. Yet, the strength of sulfuric acid is high enough so as to not chemically corrode the materials of which the equipment is made.

The temperature range in which the separation takes place should be below approximately 145° F. If the temperature is above approximately 145° F, the excess sulfonating agent continues to react with the sulfonic acid product so as to degrade or color the same. The lowest feasible temperature at which the separation can be carried out in a reasonable period of time is approximately 100° F. Therefore, the temperature range at which the separation can be carried out is approximately 100-145° F.

Another factor influencing the separation is the degree of agitation. In order to realize good separation in a relatively short period of time it is necessary to have a relatively high degree of agitation so that the sulfonic acid product and excess sulfonating agent are thoroughly mixed together to form the emulsion comprising as a continuous phase the excess sulfonating agent.

Another important factor in the rapid separation is the pressure at which the separation takes place. This is of importance in regard to the removal of the entrained gas in the mixture. This can be achieved by subjecting the mixture to a reduced pressure of approximately 100 mm. of mercury absolute pressure. At this pressure and in the temperature range of approximately 100-145° F, the entrained gas is removed. This allows rapid and complete separation of the two phases.

The equipment required to carry out separation can consist of a jacketed vessel having a removable cover and in which it is possible to realize the pressure of approximately 100 mm. absolute pressure and also in which equipment there is mixing means for thoroughly and completely agitating the sulfonic acid phase and the excess sulfonating agent phase. Such equipment can be made of alloy 20 or stainless steel such as the 316 type. Also, there should be means for adjusting the temperature to a value in the range of approximately 100-145° F. Also, in such equipment there should be means for introduc-

ing previously separated excess sulfonating agent from another batch. This means for introducing excess sulfonating agent is sometimes necessary in order to build up the volume of the sulfuric acid layer to a minimum of approximately thirty-five (35%) percent by volume.

Having presented one method for achieving the rapid separation of the sulfonating agent from the sulfonic acid there is herewith presented specific examples teaching such separation in detail. These examples, it is to be remembered, are by way of illustration only, and are not to be taken as limitations on the process and the invention.

Example I

In a batch process twenty gallons of dodecyl benzene are mixed in a jacketed vessel with approximately 12.7 gallons of twenty-two (22%) percent oleum over a time period of approximately one and one-half hours. During this mixing step the temperature of the mixture is not allowed to exceed approximately 95° F. Upon the completion of the mixing the mixture is allowed to digest for approximately one hour at a temperature not greater than about 130° F. At the end of this time the mixture is diluted with four gallons of water to form a concentration of sulfuric acid of approximately seventy-eight (78%) percent strength. At this acid concentration the spent sulfuric acid layer is approximately thirty-five (35%) percent by volume. The temperature during this step is maintained in the range of approximately 120° F. The mixture is well agitated at a reduced pressure in the range of approximately 100 mm. mercury absolute for a period of about five minutes. Then the mixture is allowed to settle and separate into a lower sulfuric acid layer and an upper sulfonic acid product. The separation is substantially complete in approximately twenty minutes. The sulfonic acid product has the following analysis:

| Component: | Percent by weight |
|---------------------|-------------------|
| Sulfonic acid ----- | 87.7 |
| Sulfuric acid ----- | 8.5 |
| Free oil ----- | 0.9 |
| Water ----- | Balance |

Example II

Twenty gallons of alkyl benzene comprising in the side chain ten to eighteen carbon atoms and 9.2 gallons of twenty-two (22%) percent fuming sulfuric acid are mixed together in a jacketed reaction vessel. The fuming sulfuric acid is added to the alkyl benzene over a time period of approximately one and one-half hours and the temperature during this period of time is not allowed to exceed approximately 95° F. Then, the mixture is allowed to digest for about one hour and the temperature is not allowed to exceed about 130° F. At the end of the digestion period 3.3 gallons of water and 4.3 gallons of seventy-eight (78%) percent sulfuric acid from a previous batch are added to form a mixture having a concentration of approximately seventy-eight (78%) percent strength sulfuric acid. The resulting mixture is thoroughly agitated at a pressure in the range of approximately 90-100 mm. mercury absolute for a period of about five minutes. During this time the temperature of the mixture is not allowed to exceed 135-140° F. Upon completion of the agitation the emulsion comprising as a continuous phase the sulfuric acid is allowed to separate into a lower layer comprising sulfuric acid and an upper layer comprising sulfonic acid product. The time of separation is approximately twenty minutes. The sulfonic acid product has the following analysis:

| Component: | Percent by weight |
|---------------------|-------------------|
| Sulfonic acid ----- | 87.3 |
| Sulfuric acid ----- | 8.7 |
| Free oil ----- | 0.7 |
| Water ----- | Balance |

Having presented our invention it is to be realized that it may be employed with many different types of organic

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compounds such as the esters of organic acids, unsaturated and saturated esters, aliphatic aromatic compounds, alcohols both saturated and unsaturated, and the like.

What we claim as our invention is:

1. In the process of producing alkyl benzene sulfonic acid from a reaction mixture comprising alkyl benzene sulfonic acid having from 10 to 18 carbon atoms in the alkyl group and excess sulfuric acid of greater than 86% concentration, said reaction mixture containing extraneous gas, the improvement of rapidly separating said alkyl benzene sulfonic acid from a substantial portion of said excess sulfuric acid by reducing the concentration of the sulfuric acid in said reaction mixture below 86% strength and providing a volume thereof of at least 35% of the total volume and by subjecting the mixture of alkyl benzene sulfonic acid and excess sulfuric acid to a pressure less than normal atmospheric pressure substantially to remove therefrom said extraneous gas, whereby an emulsion is formed of said alkyl benzene sulfonic acid as a discontinuous phase in said sulfuric acid of less than 86% concentration as a continuous phase, allowing the mixture rapidly to settle into its phases and separating the phases from each other.

2. In the process of producing alkyl benzene sulfonic acid from a reaction mixture comprising alkyl benzene sulfonic acid having from 10 to 18 carbon atoms in the alkyl group and excess sulfuric acid of greater than 86% concentration, said reaction mixture containing extraneous gas, the improvement of rapidly separating said alkyl benzene sulfonic acid from a substantial portion of said excess sulfuric acid by adding water to the reaction mixture containing the same to reduce the concentration of the sulfuric acid therein below 86% strength and providing a volume thereof of at least 35% of the total volume and by subjecting the aqueous mixture of alkyl benzene sulfonic acid and excess sulfuric acid to a pressure less than atmospheric pressure substantially to remove therefrom said extraneous gas, whereby an emulsion is formed of said alkyl benzene sulfonic acid as a discontinuous phase in said sulfuric acid of less than 86% concentration

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as a continuous phase, allowing the mixture rapidly to settle into its phases and separating the phases from each other.

3. In the process of producing alkyl benzene sulfonic acid from a reaction mixture comprising alkyl benzene sulfonic acid having from 10 to 18 carbon atoms in the alkyl group and excess sulfuric acid of greater than 86% concentration, said reaction mixture containing extraneous gas, the improvement of rapidly separating said alkyl benzene sulfonic acid from a substantial portion of said excess sulfuric acid by adding water to said reaction mixture with agitation to reduce the concentration of the sulfuric acid therein below 86% strength and providing a volume thereof of at least 35% of the total volume, subjecting the aqueous mixture of alkyl benzene sulfonic acid and excess sulfuric acid during said agitation to a pressure less than atmospheric pressure substantially to remove therefrom said extraneous gas while maintaining the temperature of the aqueous mixture within the range of about 100° to 145° F., whereby an emulsion is formed of said alkyl benzene sulfonic acid as a discontinuous phase in said sulfuric acid of less than 86% concentration as a continuous phase, allowing the mixture rapidly to settle into its phases and separating the phases from each other.

4. The process of producing alkyl benzene sulfonic acid as set forth in claim 3, wherein the pressure to which the aqueous mixture is subjected is about 90-100 mm. of mercury absolute.

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