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SULFONATION OF FATTY ACIDS

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This invention relates to the sulfonation of fatty acids, and more particularly to continuous sulfonation of fatty acids using 100% sulfur trioxide.

The advantages of using 100% sulfur trioxide have been recognized, but because of problems associated with the use of concentrated trioxide, the processes heretofore employed have employed extremely diluted trioxide in air, thereby requiring expensive auxiliary equipment and instrumentation. Attempts to sulfonate fatty acids using 100% sulfur trioxide vapor have been unsuccessful, the product being unsatisfactory as a sulfonic acid to have an acceptable color. In such prior attempts, diluted sulfur trioxide vapor was atomized to avoid local charring and overheating due to the high exothermic heat generated, but in such cases, the local charring and overheating could not be avoided and the product failed to have an acceptable color.

An object of the present invention is to provide a process overcoming the above-described difficulties and effectively sulfonating fatty acids with 100% sulfur trioxide and with substantial yields of a high quality product.

A further object is to provide a continuous process in which the fatty acids are sulfonated with 100% sulfur trioxide. Other specific objects and advantages of the invention will appear as the specification proceeds. I have discovered that if a liquid fatty acid, preferably in the presence of its solvent, is atomized and the resulting mist of particles discharged through sulfur trioxide vapor so that the contact time is very brief, local concentrations of sulfur trioxide are avoided and there is a minimum of local overheating and product degradation. Further, the process may be operated continuously with yields in the range of 80% and higher, while obtaining a high quality product with good color.

In one embodiment of the invention, a fatty acid, preferably in a solvent therefor, is atomized, and the resulting fine particles passed through a confined body of sulfur trioxide vapor, the sulfonated fatty acid being collected and processed for the separation of the solvent and the subsequent purification of the sulfonated product. In the foregoing process, I prefer to recycle a portion of the liquid product to the atomization and discharge steps in which contact is made with the sulfur trioxide vapor.

In a preferred operation, the fatty acid in its solvent is heated to a temperature in the range of about 125-160°F., and the liquid atomized within a chamber containing sulfur trioxide vapor, the fine fatty acid particles being discharged at a very high velocity through the vapor so that contact time is very short (fraction of a second or so). Any means for atomizing the liquid fatty acid may be employed since it is only necessary to break up the liquid into a mist of particles and to move the particles at a substantial speed through the sulfur trioxide vapor body.

The sulfur trioxide vapor may be formed by any suitable means. If desired, the sulfur trioxide may be vaporized in a steam heated vaporizer, an electric vaporizer, any other suitable vaporizer. The sulfur trioxide may be introduced into a chamber so as to form a body of vapor and the fatty acid solution may be discharged as a mist so as to pass through the body of vapor.

Any suitable solvent may be employed which will main-

tain the fatty acid in a liquid state at the reaction temperature. The use of solvent with the fatty acid depends upon the melting point and solubility of the acid so that the solvent will assure a liquid fatty acid state at the reaction temperature. A further purpose of the solvent is to prevent local overheating and subsequent darkening of the fatty acid and the reaction product. Perchloroethylene, carbon tetrachloride, and other known solvents may be employed.

The sulfur trioxide vapor is introduced through line 17 where the liquid acid is discharged between spaced disks forming a rotor head 16. The rotor head is driven by motor 14 and the liquid enters the channel of the rotor mechanism through line 15. The sulfur trioxide vapor is introduced through line 17 into a distributor 18 having openings through which the vapor is discharged to substantially fill the upper portion of the closed shell 19. The sulfur trioxide vapor forms a mist as it emerges from the rotor head 16 as indicated by the arrows 26, and the vapor exits through an outlet pipe 21 having its opening above the liquid acid body 22. The liquid mist, on emission from the rotor head 16, passes through the trioxide vapor and impinges on the walls of the shell 19, from which it flows to the liquid body 22 therebelow. The velocity of the liquid mist is such that less than a second is required to impinge it upon the shell.

The exothermic heat of reaction is removed by means of a cooling water jacket 23 extending about the shell 19. If desired, a thermocouple may be carried by the shell 19 for indicating the outside shell temperature. Liquid may be recycled from the liquid body 22 through the line 24 by means of pump 25 and through flow control 26 back to the feed line 15.

The reacted product may be withdrawn through outlet 27 and pipe 28 to the aging tank which is preferably maintained at a reaction temperature, the product being held for an additional period such as one hour before transferring it to the crystallizer. The sulfonated fatty acid is cooled in the crystallizer and may be reduced in solubility to promote crystallization by the introduction of petroleum ether (Skelly Solv), or like solvent. Seeding may be accomplished by the addition of crystalline material to promote crystallization of super-cooled solutions.

From the crystallizer the product may be passed to a filter (not shown), washed with Skelly Solv F until free of solvent, and then vacuum dried. It will be understood that such purification or final processing steps may be varied substantially, depending upon the product desired.

The yield is found to be improved substantially by the recycling of acid from the body 22, and I prefer to recycle at a ratio of 4 or 5 to 1 in the apparatus described above, best results being obtained when the recycle ratio of the reaction mass (including the weight percentage of solvent to feed is approximately 4.5 to 1 when employing a single rotor reaction stage, as illustrated in the drawing. Yields of from about 72 to 83 weight percent, with product colors ranging from Gardner 10 to 13 (20 percent in isopropanol) were obtained.

The aging at reaction temperatures was found to improve yields in both batch and continuous operations and
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for periods of about 1/2 to 3 hours, best results being obtained at about 1 hour.

While in the apparatus described above, a single rotor was employed, it will be understood that multiple rotor stages may be used for increasing throughput and for shortening the operation periods.

Specific examples illustrative of the process may be set out as follows:

EXAMPLE I

A 21 percent solution of commercially pure stearic acid in perchloroethylene was heated by a steam coil in the tank, as shown in the drawing, to a temperature of about 132° F. and discharged through the rotor head in the form of a fine mist at a high velocity. Sulfur trioxide vapor in a concentration of 39 percent in air and at a temperature of about 92° F. was discharged at the rate of 0.10 pound per minute into the shell 19, as shown in the drawing, the shell having a temperature of about 103° F. The vented gases from the shell had a temperature of 114° F.

The liquid feed and solvent were introduced into the atomizer or rotor head 16 at a rate of 1.65 pounds per minute, and liquid product from body 21 was recycled at a ratio of 6.7 to 1. The temperature in the receiver or aging tank 29 ranged between 140° and 158° F. and held a total weight of 182 pounds. The digestion temperature was approximately 135° F. The crystallization temperature was about 90° F. and the yield was 81 percent by weight of theory. The assay results were as follows:

Assay

A.V. total ........................................ 306
A.V. SO₃H ........................................ 160
A.V. COOH ........................................ 146
GA (20%) color ................................... 15

EXAMPLE II

The process was carried out as described in Example I except as to the following conditions:

The feed rate for the fatty acid and solvent was 1.62 pounds per minute at a temperature of 142–150° F., the sulfur trioxide vapor was introduced at the rate of 0.10 pound per minute and at a concentration of 100 percent SO₃. The vapor temperature was 113° F. The shell temperature was 114–116° F. The temperature of the vent gases was 104–100° F. The ratio of the recycled feed was 4.6 to 1, the recycled product having a temperature of 118–122° F. The temperature of the product in the receiver or aging tank was 142–156° F. and the total weight was 178 pounds. The digestion temperature was 135° F. and the crystallization temperature 76° F. The yield was 78.9 percent by weight, and the color was Gardner 12.

EXAMPLE III

The operation was carried out as described in Example I except that the feed rate was increased to 2,533 pounds per minute. The sulfur trioxide feed rate was 0.157 pound per minute. The sulfur trioxide concentration was 100 percent and the temperature was 113° F. The shell temperature was 114° F. and the temperature of the vent gases was 105–110° F. The recycle ratio was 4.5 to 1 of the reaction mass (including solvent) to feed, the temperature of the recycled product being 122–128° F.

The weight of the total material in the aging tank was 187 pounds, having a temperature of 125–128° F. The digestion temperature was 140° F. The crystallization temperature was 75° F. The yield was 72.2 percent by weight, and the color was Gardner (20 percent in isopropanol) 11–12.

EXAMPLE IV

The process was carried out as described in Example I except that the feed rate of the liquid acid and solvent was 2.56 pounds per minute at a temperature of 148–158° F. The sulfur trioxide was 100 percent in concentration and was fed at a rate of 0.171 pound per minute, having a vapor temperature of 113° F. The shell had a temperature of 114° F., and the vent gases had a temperature of 105–110° F. The recycle ratio was 4.47 to 1, the recycled product having a temperature of 130–150° F. There was a total of 184 pounds in the receiver (aging tank) at a temperature of 122–125° F. The digestion temperature was 138° F., and the crystallizing temperature 80° F. The yield was 72.2 weight percent, and the color was Gardner (20 percent in isopropanol) 12–13.

While in the foregoing specification I have set forth illustrative operations in considerable detail for the purpose of illustrating the invention, it will be understood that such detail or details may be varied widely by those skilled in the art without departing from the spirit of my invention.

I claim:

1. In a process for sulfonating saturated, unsubstituted fatty acids having from about 12 to 22 carbon atoms, the steps of introducing into a confined zone a body of 100 percent sulfur trioxide vapor in the upper portion of said zone, dissolving a feed fatty acid in a solvent to form a free-flowing liquid, atomizing said liquid into mist particles, passing said particles through and beyond said vapor body, and collecting said particles in a liquid body below said vapor body.

2. The process of claim 1 in which the fatty acid is selected from a group consisting of stearic, palmitic, lauric and myristic acids.

3. The process of claim 1 in which said liquid is recycled at a ratio of about 4 to 5 parts of the recycled liquid to one of said feed acid.

4. The process of claim 1 in which the liquid product is withdrawn from said liquid body and aged in a reaction zone at a temperature of about 120–150° F. for about one-half to three hours.

5. A process for sulfonating saturated, unsubstituted fatty acids having from 12 to 22 carbon atoms in their hydrocarbon radical in which a fatty acid is dissolved in a solvent to form a free-flowing liquid and contacted with sulfur trioxide vapor, characterized in that the sulfur trioxide vapor is maintained in a substantially uniform body in an upper portion of a reaction zone and said fatty acid and solvent are atomized into mist particles and the particles passed through said vapor body and collected free of said vapor in a liquid body below said vapor body in the reaction zone.

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