United States Patent Office 2,878,271
Patented Mar. 17, 1959

2,878,271

NEUTRALIZATION OF SULFONATION MIXTURES AND PRODUCTS THEREOF

William S. Little, Idaho Falls, Idaho, and Leonard M. Wylie, Atlanta, Ga., assignors to Tennessee Corporation, New York, N. Y., a corporation of New York

No Drawing. Application May 17, 1957
Serial No. 659,768

5 Claims. (Cl. 260—400)

This invention relates to processes for the improvement of the color of neutralized sulfonated unsaturated fatty acids and more particularly to such processes in which the unsaturated fatty acids contain from ten to eighteen carbon atoms and at least one double bond and are sulfonated by reaction with liquid SO_3 in liquid SO_2.

The suffonation of unsaturated fatty acids and subsequent neutralization thereof by a suitable base to provide surface active agents is known and these surface active agents have many known useful properties such as detergents and as wetting agents in the textile field.

U. S. Patent No. 2,743,288 describes processes for obtaining these surface active agents and their uses. The neutralized sulfonated fatty acids obtained by procedures such as those described in U. S. Patent No. 2,743,288 are usually of a dark brown to reddish brown color and such dark colors are undesirable for many uses.

In the textile field, for example, such surface active agents should be as light in color as possible, preferably yellow to light straw so as not to impair the color of the textiles upon which the surface active agent is being used.

It is accordingly the principal object of the present invention to provide novel processes for improving the color of neutralized sulfonated fatty acids in which the resulting products are of lighter color than has heretofore been obtained.

It is believed that the color of the neutralized sulfonated fatty acid develops with exposure time in the presence of a strong acid and to a somewhat lesser degree in the presence of a dilute acid and that the color formation is probably due to a reaction of the sensitive fatty acids such as oxidation thereof.

Most unexpectedly, we have found that the color of neutralized sulfonated fatty acids can be greatly improved and changed from dark brown or reddish brown to light yellow or to light straw color by a two-step neutralization of the sulfonation mixture as will be more fully desribed hereinafter. In accordance with our two-step neutralization procedure, the aqueous solution of the fatty acid sulfonated with an SO_2 solution of SO_3 is discharged from the SO_2 evaporator in known manner with the anhydrous sulfonated acid reaction mixture at a temperature of from 25–50° F. and containing up to 30% by weight of SO_2. The anhydrous sulfonated acid may then be mixed with a suitable amount of water and enough base is added to the acid mixture to adjust the pH of the mixture to within the range of approximately 1–4.3 and preferably in the approximate range of 2–2.5. SO_2 is stripped from the partially neutralized reaction mixture and after completion of stripping the mass is neutralized to a pH of approximately 6. The resulting neutralized sulfonated fatty acid has a light yellow color as compared to prior known colors of from dark brown to reddish brown.

As noted above, the unsaturated fatty acid should contain from ten to eighteen carbon atoms and should contain no functional groups which will react with SO_3 other than double bonds. Fatty acids coming within the scope of the present concept are, but are not limited to undecylenic, palmitolic, oleic, linoleic, linolenic and vaccenic.

The temperature at which the sulfonated mixture is discharged from the SO_2 evaporator will depend upon the base which is employed in the subsequent partial neutralization step and this temperature falls usually within the range of 25 to 50° F. The upper end of this temperature range may be employed when the base is sodium hydroxide, potassium hydroxide or sodium bisulfite and when the base is an amine the upper limit of the temperature range may be dropped to approximately 40° F. to obtain good color. For example, if the reaction mixture is heated above 40° F. before triethanolamine is added the color of the resulting product is appreciably darker.

In the partial neutralization step, the sulfonated mixture from the SO_2 evaporator is partially neutralized by the addition of a base to a pH range of from 1 to 4.3 and preferably in the pH range of approximately 2–2.5 depending upon the base which is employed. For example, if sodium bisulfite is employed as the base, higher pH's can be employed since sodium bisulfite is stable at such higher acidities, it being understood that the less stringent acid conditions give better color in the end product and the heat of reaction distributed uniformly throughout the mixture gives better internal heat for stripping SO_2.

As noted above, sodium hydroxide, potassium hydroxide and sodium bisulfite are suitable bases for use in our novel processes and any aliphatic amine which boils at room temperature or higher is also satisfactory as a base for use herein. These amines include but are not limited to aliphatic amines which boil at room temperature or higher are also satisfactory as for use herein. These amines include but are not limited to aliphatic primary, secondary and tertiary amines including triethanolamine, monoethanolamine, diethanolamine, di-n-butylamine, diethylamine, isopropylamine and 2-ethylhexylamine.

The following examples are illustrative of processes in accordance with the present invention for improving the color of neutralized sulfonated fatty acids and of the novel products thereof but should in no way be construed as defining or limiting the present concept, reference being had to the appended claims to determine the scope of this invention:

Example 1

123 pounds of an oleic acid containing 5% polyunsaturates and 8% saturated fatty acid were placed in a closed, jacketed, agitated, 150 gallon vessel. An SO_2-SO_3 solution, maintained at 14° F. or less, containing 40.13 pounds of SO_3 and 602 pounds of SO_2 was added to the reactor containing the oleic acid in 10 minutes with no external heating or cooling on the vessel. The temperature of the reaction mass during reaction dropped from the ambient temperature to 14–20° F. The liquid SO_2 remaining after reaction was removed, condensed and stored. After heating the reaction mass for 58 minutes by circulating 110–115° F. water through the reactor jacket, a reactor temperature of 32° F. was reached. The reactor was opened and air pulled over the reaction mass to scavenge SO_2 being evolved. The circulating water was cut off and the jacket drained.

128.47 pounds of water at 84° F. were added in 7 minutes and the reaction mixture was agitated for 3.5 minutes. At this point 82.5% (18.7 pounds as a 43.5% solution) of the theoretical sodium hydroxide required for neutralization of the sulfonic acid and H_2SO_4 formed was added in 15 minutes, controlling the height of foam due

to evolution of SO_2 by the rate of addition of sodium hydroxide solution. The initial pH after completion of the caustic addition was approximately 2, while the reaction mass temperature rose to 150° F. Stripping of SO_2 was continued for 63 minutes with no external heat supplied. After completion of stripping, the mass was neutralized to a pH of 6 with 24.8 pounds of 43.5% NaOH and the product heated at 190–195° F. for 90 minutes to hydrolyze any sulfate groups present.

The product had the following analysis:

H_2O	percent	48.0
Oil	do	4.8
Inorganic	do	3.18
SO_2	do	0.5
Active	do	43.52
Color, Gardner		9

When the SO_2 content of the reaction mass was reduced to about 1% before any base was added, the color of the product was about 12 on the Gardner scale.

Example 2

192.2 pounds of an oleic acid containing 5% polyunsaturates and 8% saturated fatty acid were placed in a closed, jacketed, agitated, 150 gallon vessel. An SO_2-SO_3 solution, maintained at 14° F. or less, containing 62.64 pounds of SO_3 and 940 pounds of SO_2 was added to the reactor containing the oleic acid in 17½ minutes with no external heating or cooling on the vessel. The reaction mass temperature during reaction dropped from the ambient temperature to 14–20° F. The liquid SO_2 remaining after reaction was removed, condensed and stored. After heating the reaction mass for 103 minutes, by circulating 110–115° F. water through the reactor jacket, a reactor temperature of 36° F. was reached. The reactor was opened to the atmosphere and air pulled over the reaction mass to scavenge SO_2 being evolved. The circulating water was cut off and the jacket drained.

At this point 90% (118.8 pounds) of the theoretical triethanolamine required for neutralization of the sulfonic acid and H_2SO_4 formed was added in 13.5 minutes, controlling the height of foam rise by the addition rate. Immediately following the triethanolamine addition, 12 pounds of water to hydrolyze sulfate groups present was added in ½ minute. The temperature at completion of triethanolamine and water addition was 182° F. The pH of the mass was 2.3. The partially neutralized mass was then heated with steam for 5 hours at a temperature of 180–190° F. to strip absorbed SO_2. The remainder of the theoretical triethanolamine plus 17% excess (total 35.5 pounds) was added to raise the pH of the final product to 5.7.

The product analyzed as follows:

Oil	percent	5.3
SO_2	do	0.6
H_2O	do	2.0
Active	do	82–85
Inorganic	do	7–10
Color, Gardner		10.5

When the SO_2 content of the reaction mass was lowered to 1–2% before any base was added, the color of the final product was about 15 on the Gardner scale.

Example 3

132 pounds of a tall oil fatty acid containing 48% linoleic acid, 50% oleic acid and 2% saturated fatty acids were placed in a closed, jacketed, agitated, 150 gallon vessel. An SO_2-SO_3 solution, maintained at 14° F. or less, containing 43 pounds of SO_3 and 645 pounds of SO_2 was added to the reactor containing the tall oil fatty acid in 10.7 minutes with no external heating or cooling on the vessel. It was necessary to maintain a 27 at which its potential balances that applied to the contact 28 by the unit 22 as determined by the energization pressure of 14–16 p. s. i. g. on the reactor during reaction and also during evaporation of residual SO_2 to prevent the reaction mass from foaming to such an extent that the reactor and vapor lines to the SO_2 condenser would be completely filled and the condenser fouled. Evaporation was effected by circulating 110–115° F. water in the jacket for 86 minutes until a pot temperature of 56° F. at 14 p. s. i. g. was reached. The SO_2 evaporated was condensed and stored for reuse. The reactor was blown down to atmospheric pressure and opened in 4 minutes. Air was pulled over the reaction mass to scavenge SO_2 being evolved. The circulating water was cut off and the jacket drained.

146.57 pounds of water at 112° F. was added in 20 minutes and the mass agitated for 3 minutes. 82.5% (40.1 pounds of 50% solution) of the theoretical sodium hydroxide required for neutralization of the sulfonic acid and H_2SO_4 formed was added in 12 minutes to give a pH of 2. The temperature rose to 125° F. Stripping was continued for 90 minutes using steam to maintain a temperature of 130–140° F. The partially neutralized reaction mass was neutralized to a pH of 6 by adding 23.1 pounds of 50% sodium hydroxide and the product heated at 190–195° F. for two hours to hydrolyze any sulfated groups present.

The product analyzed as follows:

H_2O	percent	46.0
Oil	do	6.0
SO_2	do	0.6
Inorganic	do	1.9
Active	do	[1] 46.1
Color, Gardner		10.5

[1] By difference.

When the SO_2 content of the reaction mass was reduced to 1–2% before adding any base, the color of the product was >15 on the Gardner scale.

Example 4

125 pounds of a tall oil fatty acid containing 48% linoleic, 50% oleic and 2% saturated fatty acids were placed in a closed, jacketed, agitated, 150 gallon vessel. An SO_2-SO_3 solution, maintained at 14° F. or less, containing 40.38 pounds of SO_3 and 606 pounds of SO_2 was added to the reactor containing the tall oil fatty acid in 11.5 minutes, maintaining a pressure of 14–16 p. s. i. g. on the reactor to prevent foaming. Evaporation of residual SO_2 was effected by circulating 110–115° F. water in the jacket for 81 minutes until a pot temperature of 52° F. at 10 p. s. i. g. was reached. The SO_2 evaporated was condensed and stored for reuse. The reactor was blown down to atmospheric pressure and opened in 3 minutes. Air was pulled over the reaction mass to scavenge SO_2 being evolved. The circulating water was cut off and the jacket drained. Agitation was continued for 6 minutes, at which time 90% (70.1 pounds) of the theoretical triethanolamine required for neutralization of the sulfonic acid and H_2SO_4 formed was added in 12.0 minutes. The initial temperature was 35° F. and the final temperature of 162° F., while the pH was 2.5. The foam height during addition of triethanolamine was controlled by varying the rate of triethanolamine addition. After stirring 3.5 minutes, 7.8 pounds of water was added in 1 minute to hydrolyze sulfate groups present.

The partially neutralized mass was heated with steam for 5 hours at 190–220° F. to strip absorbed SO_2. The remainder of the theoretical triethanolamine plus 20% excess (total 32 pounds) was added to raise the pH of the final product to 5.8.

The product analyzed as follows:

Oil	percent	8.5
SO_2	do	0.7
H_2O	do	0.9
Active	do	82–85
Inorganic	do	7–10
Color, Gardner		11

When the SO_2 content of the reaction mass was reduced to 1–2% before adding any base, the color of the product was about 17 on the Gardner color scale.

It should now be apparent to those skilled in the art that the processes herein described in every way satisfy the objective stated above and provide novel neutralized sulfonated fatty acids of improved color ranging from light yellow to light straw, which are particularly useful as surface active and wetting agents in the textile industry.

Changes in or modifications to the above described illustrative processes may now be suggested without departing from the present inventive concept. Reference should be had to the appended claims to determine the scope of this invention.

What is claimed is:

1. In a process in which an unsaturated fatty acid is reacted with an SO_2-SO_3 solution, the steps of heating the reaction mixture until it reaches a temperature in the range of approximately 25–50° F., removing SO_2 as evolved, adding a base to the reaction mixture until the pH of the reaction mixture is in the approximate range of from 1–4.3, and preferably in the approximate range of 2–2.5, continuoutly removing evolved SO_2 and after removal of SO_2 adding additional base to the stripped reaction mixture until the pH of the mixture is approximately 6.

2. In a process, the steps of reacting an unsaturated fatty acid containing 10–18 carbon atoms with an SO_2-SO_3 solution, distilling off unreacted liquid SO_2, maintaining the temperature of the reaction mixture in the range of approximately 25–50° F., removing evolved SO_2, adding a base selected from the group consisting of sodium hydroxide, potassium hydroxide, sodium bisulfite, an aliphatic primary amine, an aliphatic secondary amine and an aliphatic tertiary amine to the reaction mixture until the pH of the reaction mixture is in the approximate range of 1–4.3, and preferably in the approximate range of 2–2.5, continuously removing evolved SO_2 and after removal of SO_2 adding additional base to the stripped reaction mixture until the pH of the reaction mixture is approximately 6.

3. In a process, the steps of reacting a fatty acid from the group consisting of undecylenic, palmitolic, oleic, linoleic, linolenic and vaccenic with an SO_2-SO_3 solution, distilling off liquid unreacted SO_2, maintaining the temperature of the reaction mixture in the approximate range 25–30° F. and scavenging evolved SO_2 in a current of air, adding a base selected from the group consistin gof sodium hydroxide, potassium hydroxide, sodium bisulfite, triethanolamine, monoethanolamine, diethanolamine, di-n-butylamine, diethylamine, isopropylamine and 2-ethylhexylamine to the reaction mixture until the pH of the reaction mixture is in the approximate range 1–4.3, and preferably in the approximate range 2–2.5, continuously removing evolved SO_2 and then after removal of SO_2 adding additional base to the stripped reaction mixture until the pH of the reaction mixture is approximately 6.

4. A process as described in claim 3 in which the sulfonated reaction mixture before partial neutralization contains approximately 30% SO_2 and the neutralized sulfonated reaction mixture contains approximately .5 to .7% SO_2.

5. A process as described in claim 3 including the step of heating the neutralized sulfonated reaction mixture with addition of necessary water to a temperature in the approximate range of 190–195° F. to hydrolyze sulfate groups.

References Cited in the file of this patent

UNITED STATES PATENTS

2,195,145 Crittenden ---------- Mar. 26, 1940

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,878,271 March 17, 1959

William S. Little et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 53, for "desribed" read -- described --; column 2, line 36, after "as" insert -- bases --; line 54, for "So_3" read -- SO_3 --; column 4, lines 3 and 4, strike out "27 at which its potential balances that applied to the contact 28 by the unit 22 as determined by the energization"; column 5, line 32, for "continuoutly" read -- continuously --; column 6, line 17, for "sistin gof" read -- sisting of --.

Signed and sealed this 11th day of August 1959.

(SEAL)
Attest:
KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents