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PROCESS FOR PREPARING SALT-FREE ORGANIC SULFONATE DETERGENTS

John Ross, Ramsey, N. J., assignor to Colgate-Palmolive Company, Jersey City, N. J., a corporation of Delaware

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The present invention relates to a process for preparing organic sulfonate synthetic detergent compositions and has particular reference to an improved process for preparing organic sulfonate synthetic detergent compositions having a high content of active ingredient.

In the preparation of organic sulfonate synthetic detergents containing water-soluble salts of sulfated and sulfonated organic materials as the active ingredient a considerable excess of sulfonating agent is generally used and the unreacted portion is subsequently neutralized along with the organic sulfonate. For example, in the preparation of sulfonated organic material using an excess of sulfuric acid or oleum as the sulfonating agent, the excess appears in the neutralized product as sodium sulfate when a sodium compound is used for neutralizing the sulfonated mixture.

Neutralization of sulfonation reaction mixtures yields a product containing a large proportionate amount of inorganic sulfate and a correspondingly low proportionate amount of organic sulfonate salt or active ingredient. For example, synthetic detergents containing water-soluble salts of sulfuric acid esters of monoglycerides of fatty acids as the active ingredient are generally prepared by subjecting fatty oil and glycerine, in proportional amounts to form the monogylceride, to the action of oleum and neutralizing the sulfonated mixture. Oleum is used in considerable excess of the stoichiometric amount required to effect the sulfonation and increase the yield of active ingredient. Upon neutralization of the resultant acid mixture with sodium hydroxide and spray drying the product to remove water, a water-soluble detergent composition in particulate form is produced which consists chiefly of about 30 to 40% by weight of organic sulfonate (sodium salt) as the active ingredient and about 60 to 70% by weight of sodium sulfate. Such a composition has been found to be an excellent detergent for certain industrial and household uses, but for some purposes it is desired to provide a product having a higher percentage of active ingredient than that obtained in the process described. To accomplish this, it has been the practice heretofore to extract the active ingredient with a suitable solvent, e. g. a short-chain aliphatic alcohol. This procedure, however, involves extra operations and requires a relatively large amount of an extracting solvent as well as additional equipment and storage facilities, all of which increase the cost of producing the detergent.

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Attempts have also been made to reduce the inorganic salt content of the final product by diluting the acid reaction mixture with water or an aqueous solution of sodium sulfate in order to cause said mixture to separate into a plurality of immiscible liquid layers in which the organic sulfonates and the excess sulfonating agent appear in different liquid layers whereby the same may be separated therefrom. Such processes have certain disadvantages and limitations which lessen their desirability for industrial operation inasmuch as said liquid phase separation occurs very slowly and incompletely. Furthermore, due to an evolution of heat resulting from the dilution of the acid mixture with water, the resultant product is of a poor quality due to being mixed with decomposition products produced as a result of hydrolysis of the sulfonated material.

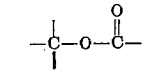
It has now been discovered that these disadvantages and limitations may be overcome or substantially minimized by separating excess sulfonating agent from a sulfonation reaction mixture containing an organic sulfonic acid by treating said mixture, in the presence of gaseous carbon dioxide, with a neutralizing agent selected from compounds of metals of the group consisting of sodium, potassium, ammonium, magnesium and lithium. Said neutralizing agent is introduced in an amount within a range of about 5 to 15% of the amount required to completely neutralize the sulfonation reaction mixture to cause a foamy organic sulfonic acid phase to separate from an unreacted sulfonating agent phase as immiscible liquids. Neutralizing agents which may be utilized for this purpose comprise carbonates of a metal selected from the group hereinbefore mentioned.

Upon introduction of carbonate material (preferably in the form of an aqueous solution) into a sulfonation reaction mixture, a gaseous carbon dioxide evolution occurs which brings about a localized cooling effect within the body of said mixture and facilitates the rapid separation of said mixture into a plurality of immiscible liquid layers, one layer containing practically all of the organic sulfonic acid and another layer containing principally said excess sulfonating agent, partially neutralized. The carbon dioxide gas escapes rapidly in the form of bubbles which intimately mix with the organic sulfonate material present in the reaction mixture to form a spongy-liquid mass. Inasmuch as the density of said mass is less than that of the remainder of the reaction mixture, said mass rises rapidly within said mixture thus effecting the desired

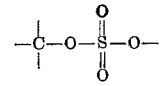
liquid-liquid separation. After the lower layer containing the sulfonating agent has been removed from the acid mixture, the organic sulfonate material contained in the upper layer may be completely neutralized by the addition of alkaline material such as caustic soda or the like to produce a detergent product containing organic sulfonate salt as the active ingredient. By this method the proportionate amount of active ingredient present in the finished product may be increased substantially above 40% by weight without causing detrimental hydrolytic side reactions as described.

The process of the present invention is applicable to sulfonation reaction mixtures containing an organic sulfonic acid and excess sulfuric acid. Among the better known types of such sulfuric acid reaction products are materials having surface modifying properties such as deterging, emulsifying, penetrating and wetting agents. Deterging agents usually have an alkyl substituent containing from about 8 to 24 carbon atoms per molecule, those containing 10 to 18 carbon atoms having particularly useful detersive properties. Representative compounds which may be suitably employed include the sulfuric acid esters of (1) long chain alcohols such as may be prepared by the reduction of higher fatty acids, e. g. dodecyl alcohol; (2) polyhydric alcohols incompletely esterified with fatty acids of high molecular weight, e. g. glyceryl monolaurate; (3) monoethanolamides of coconut fatty acids, e. g. lauric monoethanolamide; (4) higher alcohols produced by the hydrogenation of substituted phenols, e. g. alkylated or arylated phenols such as 4-octyl-2-methylcylcohexanol; (5) long chain secondary alcohols, e. g. pentadecane-2-ol; (6) low molecular weight alcohols esterified with oleic or ricinoleic acid; etc.

It is known that compounds containing carboxy ester or sulfuric acid ester linkages such as may be illustrated by the following structural formulas



and



are unstable in heated dilute aqueous solutions and/or in the presence of aqueous alkaline media owing to their tendency to hydrolyze at the carboxy ester or sulfuric acid ester linkages. Inasmuch as the rate of hydrolysis is dependent upon the temperature of the reaction mixture, e. g. being relatively rapid at temperatures above room temperature, it has been found advantageous to effect the separation of excess sulfonating agent from organic sulfonation reaction mixtures as quickly as possible and at as low a temperature as will be convenient to produce the liquid-liquid separation, e. g., at a temperature between about 20° to about 50° C., temperatures above about 50° being avoided.

In the preferred practice of the process of the invention, aqueous solutions of carbonates, bicarbonates or mixtures thereof are introduced into the sulfonation reaction mixture in an amount within the range of about 5 to 15% to cause the resulting mixture, upon stirring for two to four minutes, to separate into two layers, an upper layer which is foamy and light and readily separable containing a partially neutralized organic sulfonic acid and a lower layer of higher specific gravity consisting principally of excess sulfonating agent.

Admixing and cooling of the materials to prevent undesirable hydrolytic decomposition reactions may be suitably carried out by utilizing a shallow rotatable cup positioned centrally within a water cooled condenser having cooling wall surfaces arranged concentrically of the cup. A two phase liquid separation occurs upon the simultaneous feeding of the acid mix and aqueous carbonate solution into the shallow cup. Said cup is rotated at sufficient speed to cause the two-phase liquid mixture to be thrown by centrifugal force against the adjacent cooling wall surfaces of the condenser. The liquid mixture flowing down the walls of the condenser is thus in the form of a thin film from which the heat of dilution may be quickly dissipated. In a test run, employing such an arrangement wherein sulfated lauryl alcohol was treated with sodium carbonate solution to separate excess sulfuric acid, the material flowing from the lower end of the condenser separated in a collecting vessel as a two-phase liquid mixture from which the organic material was continuously withdrawn. Analytical determinations of the product thus produced showed that little decomposition had occurred.

Utilizing such a cooling arrangement as described for effecting a separation of excess sulfonating agent from monosulfated coconut oil fatty acid monoglycerides and employing in the one case dilute sodium hydroxide and in the other sodium sulfate instead of sodium carbonate, it was found that both sodium hydroxide as well as sodium sulfate gave a much slower rate of separation and a correspondingly poorer quality product as compared with the detergent product prepared using carbonate material to separate the sulfonating agent.

Although dilute aqueous solutions of sodium carbonate are preferably introduced into the sulfonation reaction mixture to bring about a phase separation of the sulfonating agent and organic sulfonic acid, potassium, ammonium, magnesium or lithium carbonate or bicarbonate solutions of varying strength, e. g. up to saturated solutions, may be employed for such a separation.

The process may be carried out by contacting the sulfonation reaction mixture containing organic sulfonic acid and excess sulfonating agent (e. g. sulfuric acid, oleum, etc.) with a dilute (5%) sodium carbonate solution as described or by employing a relatively concentrated aqueous alkali carbonate solution as may be desired. The alkali carbonate solution is introduced in an amount within the range of 5 to 15% to cause the sulfonating agent to separate as a lower separable liquid layer leaving an upper liquid layer containing a solution of the organic sulfonic acid. Suitable amounts, e. g. 1 to 2 volumes of said alkaline solution containing 5 grams of sodium carbonate per 100 cc. of water may be added for each volume of acid mixture, more or less being used depending upon the particular sulfonate material being treated. The aqueous alkali carbonate solution is employed principally as a washing operation and may be repeated several times in order to obtain greater operating efficiency. The process also may be carried out as a continuous counter-current washing operation if desired after which the phases may be separated in any suitable manner, e. g. by centrifuging.

As an example illustrating a method of carrying out the process of the present invention, to an acid mixture comprising monosulfuric acid esters of monoglycerides of coconut oil fatty acids, e. g. as obtained by reacting glycerine and coconut oil with fuming sulfuric acid (the oil and glycerine being present in the proportion to form the monoglyceride and the sulfuric acid being of such strength and quantity as will react and form a monosulfuric acid ester leaving an excess of sulfuric acid in the mixture) there is introduced per volume of acid mix approximately 1.3 volumes of an aqueous solution of sodium carbonate comprising by weight 5 parts of soda ash in 100 parts of water. The resultant solution is admixed and cooled in a water cooled condenser in accordance with the procedure hereinbefore described, the reaction temperature being kept below about 50° C. Upon standing for a few minutes the mixture separates into two immiscible liquid layers. After the lower layer comprising principally sulfuric acid has been drawn off the upper layer containing the partially neutralized organic sulfonic acid is neutralized with a caustic soda solution in accordance with procedures well known in the art. The resultant product is then roll-dried to produce a solid detergent composition containing approximately 61% by weight sodium salt of coconut oil fatty acid monoglycerides as the active ingredient, 29% sodium sulfate and 10% ether soluble or fat material.

Although the process of the present invention has been described with particular reference to materials which are subject to hydrolysis, e. g. sulfonated fatty acid monoglycerides of coconut oil, it will be understood that the process is applicable to the separation of sulfonated organic substances, which, although not as susceptible to hydrolysis as the sulfate esters, are nonetheless subject to the formation of undesirable colored and resinous by-products. Such materials include the alkyl aryl sulfonates which may be mononuclear or polynuclear in structure. More particularly, the aromatic nucleus may be derived from benzene, toluene, xylene, phenol, cresols, phenol ethers, naphthalene, derivatives of phenanthrene, anthracene, etc. The alkyl group may consist of such radicals as dodecyl; hexyl; octyl; nonyl; decyl; mixed alkyls derived from fatty materials, cracked paraffin wax olefins, and polymers of lower mono olefins; etc. More specific examples of suitable alkyl aryl sulfonates are the propylated naphthalene sulfonates, the mixed butyl naphthalene sulfonates, tetrahydronaphthalene sulfonates, the various butylated diphenyl sulfonates, phenylphenol sulfonates, dodecyl benzene sulfonates (e. g., essentially propylene tetramers condenser with benzene and sulfonated), etc.

The localized cooling effect and the gasification of the organic sulfonic acid produced by the evolution of carbon dioxide gas in the reaction mixture may be increased, if desired, by the addition of an inert volatile material, e. g., dichlorodifluoro methane, or similar low boiling compounds, simultaneously with the carbonate solution. This is particularly advantageous when chlorosulfonic acid is used as the sulfonating agent.

One of the principal advantages obtained through the use of carbonate materials for bringing about the desirable phase separation in accordance with the present invention is that a rapid separation of the sulfonating agent from the organic sulfonic acid is effected and a sulfonate salt may be recovered which is relatively free of inorganic sulfate as well as objectionable amounts of by-products resulting from undesirable hydrolytic and similar decomposition reactions. The invention thus provides an efficient process for preparing sulfonate detergent compositions having an increased active ingredient content by direct sulfonation and neutralization processes without the need for employing extraction methods as described. The process of the present invention also permits the production, by direct sulfonation and neutralization, of sulfonated organic materials which contain only minor amounts of inorganic salts and which may contain 60% by weight and higher proportionate amounts of organic sulfonate salt or active ingredient. Furthermore, the process of the invention results in a marked economy in the amount of alkaline material required to neutralize the sulfonic acid, and further permits the production of a detergent product directly containing a controlled amount of inorganic sulfate.

Solid detergent products are generally prepared by heating the neutralized sulfonated mass to remove water and organic solvent. For this purpose the resultant liquid product may be roll or spray dried similarly as in the making of soaps in particle form. The controlled minor amount of inorganic sulfate formed during the neutralization after removal of excess sulfonating agent may be removed or left to form a constituent part of the final product, depending upon the properties desired in the finished detergent composition.

While the process may be utilized in the preparation of certain water-soluble organic sulfonate materials and particularly ester type sulfonate compounds which are readily hydrolyzed, it will be understood that the process may also be used advantageously in the treatment of other substances wherein similar difficulties as regards hydrolysis and the formation of decomposition reaction products are present.

It will be understood that the use herein of the terms "organic sulfonate" and "organic sulfonic acid," both in the specification and in the appended claims, refers to true sulfonates as well as sulfuric acid esters and salts thereof.

What is claimed is:

1. The process of separating excess sulfonating agent from a sulfonation reaction mixture containing organic sulfonic acid and excess sulfonating agent which comprises introducing a carbon dioxide-liberating compound selected from the group consisting of carbonates and bicarbonates of sodium, potassium, ammonium, magnesium, and lithium into said reaction mixture while maintaining the temperature of the resultant mixtures below about 50° C. to cause a foamy organic sulfonic acid phase to separate from an excess sulfonating agent phase as immiscible liquids, said carbon dioxide-liberating compound being introduced into said reaction mixture in an amount within the range of about 5% to 15% of the amount required to completely neutralize the said mixture, and recovering said organic sulfonic acid phase.

2. The process of separating excess sulfonating agent from a sulfonation reaction mixture containing organic sulfonic acid and excess sulfonating agent which comprises introducing a carbon dioxide-liberating compound selected from the group consisting of carbonates and bicarbonates of sodium, potassium, ammonium, magnesium, and lithium into said reaction mix-

ture while maintaining the temperature of the resultant mixture below about 50° C. to cause a foamy organic sulfonic acid phase to separate from an excess sulfonating agent phase as immiscible liquids, said carbon dioxide-liberating compound being introduced into said reaction mixture in an amount within the range of about 5% to 15% of the amount required to completely neutralize the said mixture, recovering said organic sulfonic acid phase, neutralizing the organic sulfonic acid, and heat drying the resultant mass to produce a detergent composition containing over 60% by weight of an organic sulfonate salt as the active ingredient.

3. The process of separating excess sulfonating agent from a sulfonation reaction mixture containing organic sulfonic acid and excess sulfonating agent which comprises introducing a carbon dioxide-liberating compound selected from the group consisting of carbonates and bicarbonates of sodium, potassium, ammonium, magnesium, and lithium into said reaction mixture while maintaining the temperature of the resultant mixture between about 20° and 50° C., said carbon dioxide-liberating compound being introduced into said reaction mixture in an amount within the range of about 5% to 15% of the amount required to completely neutralize the said mixture whereby said organic sulfonic acid and excess sulfonating agent separate as immisicible liquid phases, recovering said organic sulfonic acid phase, and thereafter neutralizing the organic sulfonic acid thus obtained.

4. The process of separating excess sulfonating agent from a sulfonation reaction mixture containing organic sulfonic acid and excess sulfonating agent which comprises introducing an inert volatile material together with a carbon dioxide-liberating compound selected from the group consisting of carbonates and bicarbonates of sodium, potassium, ammonium, magnesium, and lithium into said reaction mixture while maintaining the temperature of the resultant mixture between about 20° and 50° C., said carbon dioxide-liberating compound being introduced into said reaction mixture in an amount within the range of about 5% to 15% of the amount required to completely neutralize the said mixture whereby said organic sulfonic acid and excess sulfonating agent separate as immiscible liquid phases, recovering said organic sulfonic acid phase, thereafter neutralizing the organic sulfonic acid thus obtained, and drying the resultant mass to produce a detergent composition containing over 60% by weight of an organic sulfonate salt as the active ingredient.

5. In the process of producing organic sulfonate synthetic detergent compositions containing a high content of active ingredient wherein organic sulfonation reaction mixtures containing organic sulfonic acid and excess sulfonating agent are neutralized to form water soluble organic sulfonate salts, the improvement which comprises introducing into said sulfonation reaction mixture prior to neutralization an aqueous solution containing a carbon dioxide liberating compound selected from the group consisting of carbonates and bicarbonates of sodium, potassium, ammonium, magnesium, and lithium while maintaining the temperature of the resultant mixture below about 50° C. to cause a foamy organic sulfonic acid phase to separate from an excess sulfonating agent phase as immiscible liquids, said carbon dioxide-liberating compound being introduced into said reaction mixture in an amount within the range of about 5% to 15% of the amount required to completely neutralize the said mixture, recovering said organic sulfonic acid phase, neutralizing the organic sulfonic acid thus obtained, and spray drying the resultant mass to produce a detergent composition containing over 60% by weight of an organic sulfonate salt as the active ingredient.

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