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PROCESS FOR PREPARING WETTING, SUDSING, EMULSIFYING, AND DETERGENT AGENTS

Arnon O. Snoddy and Wilfred S. Martin, Cincinnati, Ohio, assignors to The Procter & Gamble Company, Cincinnati, Ohio, a corporation of Ohio

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This invention relates to an improved process for preparing wetting, sudsing, emulsifying and detergent agents consisting of salts of sulfated higher alcohols.

Its object is to prepare these materials by using only a dry solid reagent as described below which converts the alcohol to the salt of the sulfated alcohol in a single reaction.

This application is a companion case to our application Serial No. 646,708, filed December 10, 1932 and issued as U. S. Patent No. 2,049,670 on August 4, 1936, and it is also related to our copending application Serial No. 59,789, filed January 18, 1936, which is directed specifically to preparing wetting, sudsing, emulsifying and detergent agents of exceptional efficiency from unsaturated higher aliphatic alcohols by sulfating them with a reagent prepared by the reaction of sulfur trioxide on metal chlorides or of chlorsulfonic acid on metal chlorides or sulfates.

It is well known that good wetting, sudsing, emulsifying and detergent agents can be prepared from the higher aliphatic alcohols, especially those containing from about ten to twenty-two carbon atoms per molecule in two stages, by first sulfating the alcohols and then neutralizing the sulfuric esters thus formed. In the past the sulfation reaction has always been carried out by treating the alcohols with liquid reagents, such as concentrated sulfuric acid, fuming sulfuric acid, or chlorsulfonic acid, all of which are liquids of highly corrosive nature. This reaction must be carried out in acid proof liquid-tight vessels and there is always danger from leakage or spillage in handling such liquids, and especially in carrying out the sulfation reaction itself due to frothing. The sulfuric acid esters thus formed must next be neutralized, which is usually accomplished by adding the esters to an aqueous solution of caustic alkali, another liquid of corrosive nature, which thus adds to the danger from possible leaks and spills.

We have discovered that good wetting, sudsing, emulsifying and detergent agents can be made from the higher aliphatic alcohols containing from about ten to twenty-two carbon atoms per molecule without the use of corrosive liquids either in the sulfation or neutralization steps, by treating said higher alcohols with a solid reagent in powder form, described herein, which directly converts the alcohols to the neutral salt of the sulfuric esters of the alcohols. Solvents are unnecessary in the present process. Neutralization of any excess reagent used is readily accomplished in our process by the further addition of a solid basic or alkaline reagent as described below.

The reagent which we use may be produced by causing chlorsulfonic acid to react with either the chloride or sulfate of a metal such as sodium, potassium, ammonium, cobalt, manganese, etc.

The reagent thus obtained probably consists largely of the chlorsulfonate of the metal, although its actual composition need not be definitely established. We prefer to use a metal which forms a sulfation product which is at least moderately soluble in water, sodium, potassium, magnesium, and manganese being especially desirable.

For making wetting, sudsing, emulsifying and detergent agents we use preferably those higher aliphatic alcohols containing from about ten to twenty-two carbon atoms per molecule. The higher alcohols corresponding to the fatty acid radicals of natural fats and oils, and prepared by catalytic reduction of such fats and oils, are especially to be desired for our process; coconut oil, palm kernel oil and similar oils characterized by a high saponification value are especially suitable, and are substantial equivalents for the purpose of our process and products. Alcohols obtained from other sources, such as the saponification of sperm oil and the oxidation of paraffin hydrocarbons may also be used; the latter, however, consist largely of secondary alcohols and do not make as good detergent products in general as the corresponding primary alcohols unless especially purified.

Alcohols from sperm oil are in the main unsaturated and we have in a companion application (Ser. No. 59,789, filed January 18, 1936) covered our discovery herein disclosed so far as it applies to the unsaturated alcohols. In this specification and claims the term fat includes any natural fat or fatty oil, whether of vegetable or animal origin.

In preparing our reagent we mix commercial chlorsulfonic acid with sodium chloride or sulfate or corresponding salt of other metal at room temperature. A vigorous reaction ensues with a rise of temperature, and evolution of hydrochloric acid gas when chlorides are used. The temperature is preferably kept below about 50° C., as side reactions take place at higher temperatures with evolution of chlorine in some cases. This product is also a solid in powder form, or easily reducible to a powder.

Moisture must be excluded as moisture decomposes these reaction products. An excess of the dry salt (NaCl, Na_2SO_4, etc.) in preparing the

reagent is desirable in the reagent as used, as it makes a more friable reaction mixture which is more easily mixed and ground. The excess may conveniently be from twenty-five per cent to one hundred per cent of the calculated quantity.

It will be noted that the chlorsulfonic acid is used only to react with the solid chloride or sulfate and not with the alcohol, so that no frothing of the corrosive acid occurs with its attendant danger, such as occurs when sulfating the alcohol with this reagent. Of course in the sulfation of the alcohols the reagent is a solid, so that our method has been termed a "dry" sulfation, the only fluid present being the alcohols.

Our reaction with the alcohols is carried out by adding the powdered solid reaction product, described above to the alcohol in a suitable mixing vessel of acid resistant material at an initial temperature of about 30° C. and stirring for about an hour or until the reaction ceases. The alcohol is in a liquid or molten condition at the start, so that the mixture of same with the powdered solid reagent takes the form of a thick pasty liquid at first, but becomes solid as the reaction progresses. The temperature rises, but should preferably be held below about 60° or 80° C. by suitable cooling means until the reaction is completed. Evolution of hydrochloric acid gas occurs. We preferably use an excess of the reagent amounting to one fourth to one half more than the theoretically calculated quantity in order to secure rapid and complete action. At least 90 per cent of the alcohol is sulfated under these conditions, and usually 95 or 96 per cent. In sulfating with ordinary liquid sulfating agents it is rarely possible to obtain over 90 per cent sulfation, and an excess of reagent usually causes undesired side reactions.

A ball mill, suitably constructed to provide for cooling and for removal of hydrochloric acid gas formed in the reaction, is one suitable type of mixer both for preparing our reagent and for the reaction with the alcohols, but other types may also be used. This mill serves not only for mixing but for pulverizing the products.

The reaction may be represented as follows, assuming that the $HClSO_3$-NaCl reaction product is mainly the chlorsulfonate, and R being the alkyl radical of an alcohol.

$$\underset{\text{(Alcohol)}}{ROH} + \underset{\substack{\text{(Sodium}\\ \text{chlorsul-}\\ \text{fonate)}}}{NaClSO_3} \longrightarrow \underset{\substack{\text{(Sodium}\\ \text{alkyl}\\ \text{sulfate)}}}{RNaSO_4} + HCl$$

Any excess of reagent used is subsequently neutralized by treating with a neutralizing agent consisting of finely ground metal oxide, hydroxide or carbonate in sufficient quantity to neutralize any acidity in the mixture, thus obtaining a solid product which when used in aqueous solution is found to have excellent wetting, sudsing, emulsifying and detergent properties without further purification. Of course the reaction mixture could also be neutralized by mixing with a solution or slurry of a metal oxide, hydroxide, or carbonate, especially if the product is to be used immediately in the wet condition, but the dry neutralization as described is preferable, especially if the product is to be stored or shipped. Usually the same metal would be selected for neutralizing excess reagent as was used in making the reaction product, but in any event it should be one that does not form insoluble reaction products, either when dry or when added to water for use. The neutralized excess reagent may be allowed to remain in the neutralized product, as it is harmless for ordinary uses, or it may be removed by a purification process as described below. The product, however, tends to decompose if left in an acid condition for any length of time unless protected from moisture, and should therefore be neutralized or made slightly alkaline to stabilize it. The amount of neutralizing agent thus required is much less than when the alcohol is sulfated in the usual manner with chlorsulfonic acid, for example, as in this case, all the sulfating agent used must be neutralized, including both that portion reacting to form esters and any excess of reagent present.

If a purer form of product is desired it may be treated, after neutralization with petroleum ether or other suitable organic solvent to remove unsulfated organic material; it may also be purified, either with or without previous removal of unsulfated organic material, by dissolving in ethyl alcohol or other suitable solvent of the sulfated alcohol salt, filtering from inorganic and other impurities, and the solvent then removed by evaporation.

Example 1

58 parts of sodium chloride and 58 parts of chlorsulfonic acid are mixed for about fifteen minutes or until the reaction is complete while keeping the temperature below about 50° C. in a suitable mixing apparatus and the product is ground to a powder. These proportions provide a considerable excess of sodium chloride. The pulverized solid reagent thus produced is mixed with 95 parts of a mixture of the alcohols obtained by the catalytic reduction of coconut oil by hydrogen under high pressure, said alcohols having an average molecular weight of 208. The mixture is stirred in an acid resisting vessel, while protected from moisture and keeping the mixture cooled to about 60° C., until the reaction is substantially complete. The resulting mixture is a solid which can readily be reduced to powder form. To this mixture is added solid sodium carbonate containing about 26 parts of actual sodium carbonate and thoroughly mixed. The result is a neutral or alkaline powder perfectly stable under ordinary storage conditions and whose water solutions have excellent wetting, sudsing, emulsifying and detergent properties.

Other higher aliphatic alcohols may be substituted, such as for example 110 parts of the alcohols derived from tallow by catalytic reduction, or 120 parts of the alcohols obtained from sperm oil by known methods. Also other metals than sodium or potassium may be used both in forming the sulfating reagent and in neutralizing, such metals as manganese, magnesium and nickel being especially suitable.

Example 2

71 parts of anhydrous sodium sulfate are mixed with 58 parts of chlorsulfonic acid in an acid resisting vessel while keeping the temperature below about 50° C. The solid product is pulverized and mixed with 115 parts of alcohols derived from tallow by catalytic reduction with hydrogen under high pressure. The procedure, including neutralization, is carried out exactly as in Example 1, yielding a solid product stable under storage conditions, which when dissolved in water shows excellent wetting, sudsing, emulsifying and detergent properties.

Example 3

The product of Example 1 was extracted with petroleum ether to remove organic impurities and then dissolved in ethyl alcohol, filtered, and

crystallized by evaporation of the ethyl alcohol. The product was a white, solid powder having very superior wetting, sudsing, emulsifying and detergent properties.

Our procedure affords a new reaction for preparing wetting, sudsing, emulsifying and detergent agents consisting essentially of salts of sulfated higher aliphatic alcohols, which has important advantages over the wet procedures hitherto used. The necessity or difficulty of maintaining the reaction vessel liquid-tight is greatly minimized because of the viscous to solid condition of the reacting mixture in its various stages. The sulfating operation, the neutralizing of any excess of the acid reagent used, and the final pulverizing can be carried out conveniently in the same mixing vessel. The full amount of both alcohol and sulfating reagent may be added at one time, whereas in the wet process the sulfating agent, such as chlorsulfonic acid, must be added to the alcohol slowly over a long period of time in order to keep the temperature down to the required point, while if added too slowly some of the sulfated product first formed is destroyed. The older process involves danger in that if through the breakage of a valve or other accident the acid flows into the alcohol too fast, this would cause a serious rise of temperature, resulting in undesirable side reactions and even possible explosion. We obtain a higher percentage of sulfation with greater freedom from undesired side reactions. Our process is considerably more economical than the prior processes involving first sulfating with an acid and then neutralizing with an alkali because our reagents consist of chlorsulfonic acid, sodium chloride (or sulfate) and a small amount of sodium carbonate, as compared with chlorsulfonic acid, and sodium hydroxide or carbonate. In other words, we have in effect replaced the sodium hydroxide or carbonate mainly with sodium chloride, which is much cheaper.

The product made by our process if protected from moisture even without neutralization is sufficiently stable to be allowed to rest for several days if necessary before final neutralization, whereas sulfated alcohols prepared with chlorsulfonic acid and other liquid sulfating agents are very unstable and must be neutralized immediately to prevent decomposition; they cannot even be allowed to stand over night before neutralization without serious decomposition. Our product needs no further drying, after preparation as described, but can be stored or shipped in its condition immediately after neutralizing, whereas in the usual wet process the product must be dried, which involves not only an additional expense but also a certain amount of decomposition and loss.

Having thus described our invention, what we claim and desire to secure by Letters Patent is:

1. A process for making wetting, sudsing, emulsifying and detergent agents comprising reacting an aliphatic alcohol containing ten to twenty-two carbon atoms per molecule with a solid reagent consisting of the reaction product of chlorsulfonic acid on a metal salt of the group consisting of chloride and sulfate, said metal being one which forms in the said reaction a salt of the sulfuric ester of the said alcohol which is soluble in water.

2. A process for making wetting, sudsing, emulsifying and detergent agents comprising reacting an aliphatic alcohol containing ten to twenty-two carbon atoms per molecule with a solid reagent consisting of the reaction product of chlorsulfonic acid on a metal salt of the group consisting of chloride and sulfate, the product thus obtained being neutralized by further treatment with a solid neutralizing agent selected from the group consisting of metal oxides, hydroxides, and carbonates, said metals being ones which form salts of the sulfuric ester of said alcohol which are soluble in water.

3. A process for making wetting, sudsing, emulsifying and detergent agents comprising reacting alcohols derived from a natural fat by catalytic reduction with a solid reagent consisting of the reaction product of chlorsulfonic acid on a metal salt of the group consisting of chloride and sulfate, the product thus obtained being neutralized by further treatment with a solid neutralizing agent selected from the group consisting of metal oxides, hydroxides, and carbonates, said metals being ones which form salts of the sulfuric esters of said alcohols which are soluble in water.

4. A process for making wetting, sudsing, emulsifying and detergent agents comprising reacting alcohols derived from coconut oil by catalytic reduction with a solid reagent consisting of the reaction product of chlorsulfonic acid on a metal salt of the group consisting of chloride and sulfate, the product thus obtained being neutralized by further treatment with a solid neutralizing agent selected from the group consisting of metal oxides, hydroxides, and carbonates, said metals being ones which form salts of the sulfuric esters of said alcohols which are soluble in water.

5. A process for making wetting, sudsing, emulsifying and detergent agents comprising reacting an aliphatic alcohol containing ten to twenty-two carbon atoms per molecule derived from oxidized paraffin hydrocarbons with a solid reagent consisting of the reaction product of chlorsulfonic acid on a metal salt of the group consisting of chloride and sulfate, the product thus obtained being neutralized by further treatment with a solid neutralizing agent selected from group consisting of metal oxides, hydroxides, and carbonates, said metals being ones which form salts of the sulfuric ester of said alcohol which are soluble in water.

6. A process for making wetting, sudsing, emulsifying and detergent agents comprising reacting alcohols derived from a natural fat by catalytic reduction with a solid reagent consisting of the reaction product of chlorsulfonic acid on a metal salt of the group consisting of chloride and sulfate, the product thus obtained being neutralized by further treatment with a solid neutralizing agent selected from the group consisting of metal oxides, hydroxides, and carbonates, said metals being ones which form salts of the sulfuric esters of said alcohols which are soluble in water, said neutralized product being purified by washing with a suitable organic solvent to remove unsulfated organic material.

7. A process for making wetting, sudsing, emulsifying and detergent agents comprising reacting alcohols derived from a natural fat by catalytic reduction with a solid reagent consisting of the reaction product of chlorsulfonic acid on a metal salt of the group consisting of chloride and sulfate, the product thus obtained being neutralized by further treatment with a solid neutralizing agent selected from the group consisting of metal oxides, hydroxides, and carbonates, said metals being ones which form salts of the sulfuric esters of said alcohols which are

soluble in water, said neutralized product being purified by dissolving in a suitable organic solvent, separating from insoluble inorganic and other impurities and removing said solvent by evaporation.

8. A process for making wetting, sudsing, emulsifying and detergent agents comprising reacting alcohols derived from coconut oil by catalytic reduction with a solid reagent consisting of the reaction product of chlorsulfonic acid on a sodium salt of the group consisting of chloride and sulfate, the product thus obtained being neutralized by further treatment with a solid neutralizing agent selected from the group consisting of sodium oxide, hydroxide or carbonate, said neutralized product being purified by washing with a suitable organic solvent to remove unsulfated organic material.

9. A process for making wetting, sudsing, emulsifying and detergent agents comprising reacting alcohols derived from coconut oil by catalytic reduction with a solid reagent consisting of the reaction product of chlorsulfonic acid on a sodium salt of the group consisting of chloride and sulfate, the product thus obtained being neutralized by further treatment with a solid neutralizing agent selected from the group consisting of sodium oxide, hydroxide, or carbonate, said neutralized product being purified by dissolving in a suitable organic solvent, separating from insoluble inorganic and other impurities and removing said solvent by evaporation.

10. A process for making wetting, sudsing, emulsifying and detergent agents comprising reacting an aliphatic alcohol containing ten to twenty-two carbon atoms per molecule derived from oxidized petroleum with a solid reagent consisting of the reaction product of chlorsulfonic acid on a metal salt of the group consisting of chloride and sulfate, the product thus obtained being neutralized by further treatment with a solid neutralizing agent selected from the group consisting of metal oxides, hydroxides, and carbonates, said metals being ones which form salts of the sulfuric ester of said alcohol which are soluble in water, said neutralized product being purified by washing with a suitable organic solvent to remove unsulfated organic material.

11. A process for making wetting, sudsing, emulsifying and detergent agents comprising reacting an aliphatic alcohol containing ten to twenty-two carbon atoms per molecule derived from oxidized petroleum with a solid reagent consisting of the reaction product of chorsulfonic acid on a metal salt of the group consisting of chloride and sulfate, the product thus obtained being neutralized by further treatment with a solid neutralizing agent selected from the group consisting of metal oxides, hydroxides, and carbonates, said metals being ones which form salts of the sulfuric ester of said alcohol which are soluble in water, said neutralized product being purified by dissolving in a suitable organic solvent, separating from insoluble inorganic and other impurities and removing said solvent by evaporation.

12. The process of making a wetting, sudsing, emulsifying and detergent agent, which comprises causing aliphatic alcohols characterized by the presence of molecules having from twelve to twenty-two carbon atoms each, to react with the reaction product of chlorsulfonic acid on a metal salt of the group consisting of chloride and sulfate, said metal being one which forms water-soluble products of said alcohols in said reaction.

ARNON O. SNODDY.
WILFRED S. MARTIN.