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SULFONIC ACID SURFACE ACTIVE AGENT AND METHOD OF PREPARATION

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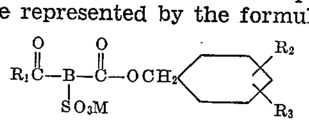
The present invention relates to novel surface active agents and more particularly, it relates to surface active agents having marked wetting properties, as well as other desirable properties, comprising a new type of chemical substance, namely, the water-soluble salts of an aroyl sulpho propionic acid ester as more fully described hereinafter. This application is a continuation in part of application Serial No. 623,438, filed November 2, 1945, and now abandoned.

The principal object of the invention is to provide surface active agents having outstanding wetting properties, which agents may be used wherever such properties are desired, for example, in processing textile fibres and fabrics, leather, paper, and other fibrous materials, in cleaning processes, such as general household cleaning, material cleaning, dishwashing, and the like, and in frothing, emulsifying, emulsion breaking, flotation, and other processes. The agents are especially useful to increase the water-absorptivity of fibrous or other materials and, therefore, the wetting agents of the invention may advantageously be used in the kier boiling of cotton, in the scouring of wool, in the boiling-off of rayon, in dyebaths, in the production of "Sanforized" cotton in the fat-liquoring of leather, in the treatment of paper, and the like.

Other objects, including the provision of a novel method of producing the wetting agents of the invention, will be apparent from a consideration of the specification and the claims.

As indicated above, the wetting agents of the present invention comprise the water-soluble salts of certain aroyl sulpho propionic acid benzyl esters, the aroyl radical being defined as a radical of the type RCO— where R is an aryl radical of the type hereinafter set forth.

The surface active agents of the present invention are represented by the formula:



where R_1 is an aryl group selected from the group consisting of phenyl; monochlorophenyl; monoalkyl phenyl and monoalkyl monochlorophenyl; the alkyl groups of which contain from 1 to 9 carbon atoms; monoalkyl tolyl, the alkyl atoms; phenyl phenyl; phenyl chlorphenyl; cyclohexyl phenyl; cyclohexyl chlorphenyl; naphthyl; monochloronaphthyl; methyl naphthyl and tetrahydronaphthyl; where R_2 is selected from the group consisting of hydrogen and alkyl groups containing from 1 to 5 carbon

atoms; where R_3 is selected from the group consisting of hydrogen and alkyl groups containing not more than 2 carbon atoms; the total number of carbon atoms in R_2 plus R_3 being no more than 5 and the total number of carbon atoms in R_2 plus R_3 plus any alkyl group on the aryl nucleus, R_1, being no more than 10; where B is an ethylene group; and where M is a cation providing water-solubility to the product.

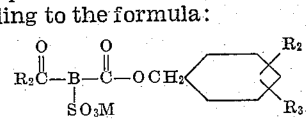
In the above formula, no attempt has been made to indicate to which of the two carbon atoms in the ethylene (B) group the sulpho group (—SO_3—M) is attached. The most practical chemical processes, however, for introducing the sulpho group into this ethylene linkage are believed to produce mixtures rather than pure alpha or pure beta derivatives. Generally, while the alpha derivative is believed to predominate, the location of the sulpho group is immaterial since it must exert a similar hydrophilic action on the molecule either in the alpha or the beta position, and it is to be understood that both the alpha and beta compounds and mixtures thereof are within the scope of the invention.

As pointed out in connection with the formula, M is a cation rendering the compound water-soluble, for example, an alkali metal such as sodium or potassium, the ammonium radical, and the like.

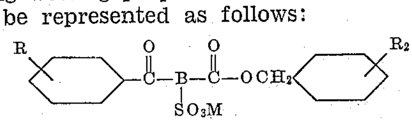
The products of the present invention thus embody not only an aroyl group but also a definite number of "exterior" or "external" carbon atoms in the various R groups. As stated, these external carbon atoms must total no more than 10. Some or all of the external carbon atoms may be provided by R_2, that is by an alkyl group containing not more than 5 carbon atoms and attached to the benzyl group or by R_2 and R_3 (totalling no more than 5 carbon atoms) when two alkyl groups are attached to the benzyl group. Some or all of the external carbon atoms may be provided by a substituted alkyl group or a substituted alkyl group and a methyl group attached to the aryl nucleus, and as indicated, these substituted groups may be an alkyl group containing from 1 to 9 carbon atoms when R_1 is monoalkyl phenyl or monoalkyl monochlorphenyl or a methyl group and an alkyl group containing from 1 to 8 carbon atoms as when R_1 is monoalkyl tolyl. It is relatively immaterial from the standpoint of the present invention whether any of the various alkyl groups mentioned is a straight or branched chain alkyl group. A chlorine atom may also be attached to the phenyl or naphthyl nucleus (as when R_1 is chlorphenyl, monoalkyl monochlorophenyl, phenyl chlorphenyl, cyclohexyl chlorphenyl or monochloronaphthyl) without altering the properties of the compound significantly. Since no one alkyl group attached to the phenyl nucleus when R_1 is monoalkyl phenyl or monoalkyl monochlorophenyl contains more than 9 carbon atoms, and since the total number of carbon atoms in R_2 plus R_3 is no more than 5, and the total number of "external" carbon atoms on the compound totals no more than 10, for each aryl group (R_1) employed, there is a definite range of carbon atoms that may be present in the groups (R_2 or R_2 plus R_3) attached to the benzyl group and vice versa. For example, if there are no alkyl groups attached to the aryl nucleus (i. e. R_1 is phenyl, monochlorophenyl, phenyl phenyl, cyclohexyl phenyl, naphthyl, monochloronaphthyl or tetrahydronaphthyl) the number of carbon atoms supplied by the alkyl group R_2 (R_3 being hydrogen) or the alkyl, groups R_2 and R_3 must be no more than 5; while if, for example, a nonyl group is attached to the aryl nucleus (i. e. R_1 is nonylphenyl or nonylchlorphenyl) R_3 is limited to hydrogen and R_2 is limited to hydrogen or a methyl group.

While numerous specific compounds may be prepared by the methods hereinafter described corresponding to the formula given for the compounds of the invention, they will possess marked wetting properties, making them available for use as surface active agents in the various industrial fields. This is because such compounds embody the basic structure hereinbefore set forth and contain external carbon atoms within the stated limits, and the specific examples hereinafter set forth demonstrate the fact that such compounds possess marked wetting properties.

The compounds of the invention possessing wetting properties to the highest degree are those corresponding to the formula:



where R_1 is monoalkyl phenyl, the alkyl group of which contains from 1 to 5 carbon atoms; where R_2 is an alkyl group containing from 1 to 5 carbon atoms; where R_3 is hydrogen; where B and M are as stated above, and where the total number of carbon atoms in R_2 plus the alkyl group attached to R_1 is from 6 to 8. To put it another way, the compounds of the invention possessing wetting properties to the highest degree may be represented as follows:



where R is an alkyl group containing from 1 to 5 carbon atoms; where R_2 is an alkyl group containing from 1 to 5 carbon atoms; where the number of carbon atoms in R plus R_2 is from 6 to 8, and where B and M are as stated. Preferably, R contains 3 to 4 carbon atoms, R_2 contains 3 to 4 carbon atoms, and M is sodium.

The products of the invention may be readily and economically prepared by condensing the desired aryl derivative reactive in a Friedel-Crafts acylation type of reaction, with the anhydride of a four carbon atom dicarboxylic aliphatic acid, i. e. maleic anhydride or succinic anhydride; esterifying the resulting acid; and then converting the ester into the sulpho derivative, as will be further discussed hereinafter. Another, but not preferred, method of preparing the products of the present invention is by condensing a half ester-half acid chloride of the four carbon atom dibasic acid with the aryl derivative to provide the ester, and then converting the ester into the sulpho derivative.

In preparing the aroyl derivative, the desired aryl derivative furnishing not only the aryl nucleus, but also any substituted alkyl group, is reacted by a Friedel-Crafts acylation reaction with a molar equivalent of the anhydride. The aryl derivative may be obtained from any source, for instance from coal tar, petroleum, or from synthetic processes. For example, in the case of alkylated phenyl derivatives, these may be obtained by condensing benzene with an alkyl halide or with an aliphatic olefin by a preliminary Friedel-Crafts alkylation reaction.

Examples of the aryl derivatives that may be used in the preparation of the aroyl derivatives in accordance with the present inventions are: benzene; monochlorobenzene; the monoalkyl benzenes such as toluene, isopropyl benzene (cumene), secondary butyl benzene, n-butyl benzene, amyl benzene, hexyl benzene, n-octyl benzene, 2-octyl benzene, 1-methyl 1-ethylamylbenzene, nonyl benzene, 1-propyl 1-methylamylbenzene, and the like; the monoalkyl toluenes such as xylene, methyl isopropyl benzene (cymene), secondary butyl toluene, octyl toluene, and the like; the monoalkyl monochlorobenzenes such as chlorotoluene, chlorocumene, secondary butyl chlorobenzene, nonyl chlorobenzene, and the like; phenyl benzene, phenyl chlorbenzene, cyclohexyl benzene, and cyclohexyl chlorbenzene, naphthalene, monochloronaphthalene, methyl naphthalene and tetrahydronaphthalene.

The anhydride of the four carbon atom dicarboxylic aliphatic acid may be the unsaturated maleic anhydride or the saturated succinic anhydride. When maleic anhydride is employed, the aroyl compound prior to sulphonation is an aroyl acrylic acid ester. Upon sulphite addition, the double bond is saturated and the product is a water-soluble salt of a aroyl sulpho propionic acid ester, wherein the SO_3M group has become attached to one of the carbon atoms of the —CH=CH— group, and a hydrogen atom to the other. In the case of succinic anhydride, the aroyl derivative of proprionic acid is formed as a result of the Friedel-Crafts reaction and a hydrogen atom attached either to the alpha or beta carbon atom must be substituted by the sulpho group, as hereinafter described.

The reaction between the aryl derivative and and the anhydride to form the corresponding aroyl acrylic or propionic acid is brought about, as has been stated above, by a Friedel-Crafts acylation reaction, and any of the various expedients used in that type of reaction may be employed in the production of the aroyl compound. Advantageously, the condensation is brought about by condensing the aryl derivative with approximately a molar equivalent of the anhydride in a suitable solvent with anhydrous or substantially anhydrous aluminum chloride. While the solvent employed may, in the case of relatively low boiling phenyl derivatives, be an excess of the phenyl derivative, the use of a suitable inert solvent such as carbon disulphide, orthodichlorobenzene, methylene chloride, ethylene chloride, and tetrachloroethane is preferred.

The aryl derivative and the anhydride may be mixed with the solvent and the aluminum chloride added thereto, preferably gradually over a period of time, or the aryl derivative may be mixed with a portion or all of the aluminum chloride and the anhydride and solvent may then be added, preferably gradually, followed by the addition of further amounts of aluminum chloride if required. Other procedures for bringing together the aryl derivative, the anhydride, the solvent, and the aluminum chloride may of course be used, if desired. For example, the aluminum chloride, anhydride, and solvent may be mixed and the aryl derivative gradually added thereto. The reaction, at least at the start, is exothermic and hydrogen chloride is evolved as the reaction proceeds. The reacting mixture is generally maintained at a temperature in the range from about 20° C. to about 65° C. by cooling at the start and by heating subsequently if necessary, and it is advantageous to agitate the mixture during the reaction.

When the condensation is completed, which may be determined by cessation of the evolution of the hydrogen chloride, the mass may be poured into ice, water, and a small amount of mineral acid, keeping the mass cold as is the usual practice in the type of reaction, and the mixture may be agitated until the aluminum chloride complex is decomposed. The condensation product which is in solution in the solvent may then be separated from the aqueous phase and washed with water and mineral acid to remove the salts of aluminum.

The aroyl acrylic or propionic acid may be isolated by either extracting it from the solvent with a warm 5% soda ash solution or by removing the solvent by distillation. The acid may be purified by disolving it in a solution of a suitable alkali, such as soda ash, filtering to remove any insoluble material and precipitating the acid by the addition of mineral acid.

In one procedure, the aryl derivative is dissolved in an inert solvent and about one molecular equivalent of maleic anhydride is added to the solution. The mixture is heated to a temperature at which the aluminum chloride complex remains dispersed, for example, to about 40° C., and is maintained between that temperature and about 50° C. during the reaction. The aluminum chloride (about 2 molecular equivalents) is added gradually, for example, in portions during the reaction, and the mass is agitated during the reaction. When the reaction is complete, which may require several hours—for example six hours—the aluminum chloride complex is decomposed and the acid isolated as above described.

In a more preferred procedure, the aluminum chloride, anhydride, and a chlorinated solvent are mixed, and the mixture is agitated and becomes uniform. The aryl derivative is gradually added at a temperature between about 40° C. and about 50° C., and after the addition is completed the mixture is stirred for a short period at a temperature between about 40° C. and about 60° C. The aluminum chloride complex is decomposed and the acid isolated as above-described.

The aroyl acrylic or propionic acid is esterified with a compound providing the desired benzyl group, and the resulting benzyl ester is then converted to the sulpho derivative. The ester of the acid may be prepared by any of the suitable esterifying reactions.

In one type of method, the ester may be formed by reacting the acid with one molecular equivalent of the benzyl alcohol containing the R_2 and R_3 groups as described corresponding to the benzyl ester desired in the presence of a solvent and an esterifying catalyst such as concentrated sulphuric acid, benzene- or toluene-sulphonic acid. Preferably, the solvent is one which like toluene, boils slightly above the boiling point of water. The mixture of the aroyl acrylic or propionic acid, the benzyl alcohol, the solvent and the esterification catalyst are boiled and the water formed by the esterification reaction is removed. After the esterification reaction has been completed, the ester, which is in solution in the solvent, may be washed with water, followed in some cases by dilute alkali to remove any unconverted acid and the traces of catalyst. The ester may be isolated by removing the solvent by steam distillation at atmospheric pressure, or by evaporation in vacuo.

In another and preferred type of esterification procedure, the benzyl ester of the aroyl acrylic or propionic acid may be obtained by dissolving the acid in a solvent such as toluene, benzene, isopropanol, ethanol, butanols, acetone, methyl ethyl ketone, dioxane, carbon tetrachloride, and the like. The acid is then converted into a salt and the desired benzyl ester formed by reaction with benzyl chloride or the appropriate alkylated benzyl chloride containing the R_2 group or the R_2 and R_3 groups as described. In such a process, the salt is advantageously formed by the addition of a slurry of soda ash in water, and in such a case, foaming occurs due to the evolution of carbon dioxide, and the mass may become thick and may have the appearance of a clear gel. The reaction between the salt of the acid and the benzyl chloride is slow and refluxing for a number of hours is generally required. When the esterification has been completed, the precipitated salt is filtered off or washed out with water and the benzyl ester is obtained upon removal of the solvent by steam or vacuum distillation.

The aroyl acrylic or propionic acid benzyl ester may be converted into the sulpho derivative by any process by which the $—SO_3—M$ group may be attached to one of the carbon atoms of the vinylene or ethylene chain of the acrylic or propionic acid ester. Preferably, when an aroyl acrylic acid ester is employed, the sulphonation is brought about by reacting the ester with a bisulphite such as sodium, potassium, or ammonium bisulphite. In the sulphonation reaction, the ester is mixed with the bisulphite dissolved in water or other solvent, for example, a mixture of equal parts of water and ethyl alcohol. The bisulphite employed is sufficient to convert the ester into the sodium or other salt of the sulphonic acid, the use of a slight excess of the bisulphite often being advantageous. The mixture is advantageously heated in a closed container equipped with an agitator until the ester becomes completely soluble in water. The temperature of heating will depend on the particular ester being treated and usually a temperature between about 80° C. and 110° C. will be employed, and in many instances it will be desirable to heat the mixture to boiling. The ester is rendered completely soluble in water by this treatment and the product formed is the sulphonic acid salt of the cation of the bisulphite. Thus, as stated in connection with the formula, —M may be any cation which provides water-solubility, for example, an alkali metal ion, ammonium radical, or the like.

Referring to the saturated aroyl propionic acid ester, it may be first converted into a halogenated derivative, for example, a bromo compound, prior to sulphonation. In such conversion process, the ester is advantageously dissolved in a solvent and a small amount of a halogenating catalyst such as phosphorus trichloride is added. The halogen, for example, bromine, is then brought into contact with the solution, for instance, by adding liquid bromine drop-by-drop to the solution. Hydrogen halide is liberated and the reation is completed in a short time. The halogenated derivative is isolated by evaporation of the solvent. The halogenated derivative thus prepared may then be sulphonated by reacting the halogen derivative with a sulphite, for example, sodium or potassium sulphite, to replace the halogen atom of the compound with the —SO_3—M group. Advantageously, the reaction is brought about by refluxing an aqueous mixture of the reactants until the reaction has progressed to completion. As in the case of the products obtained by the previously described method of sulphonation, the sulphonated product may be provided with the desired cation represented by M.

In order to illustrate the invention further, the following specific examples are given for the preparation of the compounds of the present invention. The same general procedure was employed in preparing the compounds of the examples, and is illustrated in Example 1. To avoid repetition of the details of the procedure, each of the remaining examples is set forth generally with reference back to the method of Example 1. In each case, a measure of the compound's surface activity is given by showing wetting speeds at various concentrations in water determined by the time required to wet out a 5 gram skein of raw cotton yarn at 100° F. according to the standard Draves method.

EXAMPLE 1

Preparation of the sodium salt of the isopropyl benzyl ester of secondary butyl benzoyl sulpho propionic acid

A. PREPARATION OF SECONDARY BUTYL BENZOYL ACRYLIC ACID

A mixture of 105 g. of aluminum chloride, 49 g. of maleic anhydride, and 90 ml. of 1,2-dichloroethane was stirred for 10 minutes. 67 g. (.5 mol) of secondary butylbenzene was added over a period of 15 minutes to the vigorously stirred mixture. The reactants were kept cool by immersion of the reaction flask in a bath of cold water. Agitation was continued for 90 minutes after addition of all the secondary butylbenzene. The stirring was stopped and 500 g. of crushed ice was added. The mixture was stirred cautiously and 100 ml. of 66% sulphuric acid and 50 ml. of isopropyl alcohol were then added. The mixture was stirred an additional 90 minutes, poured into a separatory funnel and the lower layer removed. The solution of secondary butyl benzoylacrylic acid was washed twice by stirring for 30 minutes with 50 ml. of 66% sulphuric acid and 50 ml. of water, followed by removal of the lower layer. The yield was 112 g. or 96.5% of the theoretical amount.

B. PREPARATION OF THE SODIUM SALT OF SECONDARY BUTYL BENZOYL ACRYLIC ACID

To the solution of the butyl benzoyl acrylic acid (approximately .49 mol) prepared above, 26.5 g. (.25 mol) of sodium carbonate dissolved in water (60 ml.) was added slowly with stirring. After a half hour, the stirring was discontinued. Approximately 1% of the acid remained unneutralized.

C. FORMATION OF THE ISOPROPYL BENZYL ESTER

To .25 mol of the sodium salt of the butyl benzoyl acrylic acid was added .25 mol (42.1 g.) of isopropyl benzyl chloride. Approximately 100 ml. of isopropyl alcohol was added and the mixture refluxed for 24 hours. The isopropyl alcohol was removed by decantation from the sodium chloride formed in the reaction. Ethylene chloride was added to aid in the decantation. The solution was heated under reduced pressure to remove all water and solvent. The temperature was allowed to reach 120° C. during this distillation. The isopropyl benzyl ester was then cooled before sulphonation.

D. SULPHONATION OF SUBSTITUTED BENZYL ESTER

To the isopropyl benzyl ester prepared above was added .25 mol of sodium bisulphite dissolved in water (70 ml.). The mixture was heated with stirring until sulphonation took place at 103° C. The stirred mixture was maintained at this temperature for an additional half hour. Any water which had been removed by distillation during the reaction was replaced, and 10 ml. of isopropyl alcohol was added. The solution was poured into a separatory funnel but no separation occurred.

The clear solution of the sulphonated ester was amber in color. The amount of active ingredient present was determined and several Draves tests were performed at various concentrations. The wetting speed at a concentration of 0.1% was only 3 seconds.

Other water-soluble salts instead of the sodium salts, such as the potassium or ammonium salts, may be prepared by employing potassium or ammonium bisulphite in the above procedure in place of sodium bisulphite. These other water-soluble salts exhibit strong surface-active properties, and may be used in a manner similar to the sodium salts.

In the following examples, the sodium salt of the benzoyl sulpho propionic acid esters is prepared, but as previously set forth, other water-soluble salts such as the potassium or the ammonium salts may be prepared by analogous procedures.

EXAMPLE 2

The salt of the methyl benzyl ester of benzoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing benzene with maleic anhydride. The benzoyl acrylic acid thus formed was converted to its sodium salt and esterified by reaction with methyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. At a concentration of 0.1%, the compound gave a wetting speed of 300 seconds, and at 0.25% a wetting speed of 40 seconds.

EXAMPLE 3

The salt of the methyl butyl benzyl ester of benzoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing benzene with maleic anhydride. The benzoyl acrylic acid thus formed was converted to its sodium salt and esterified with methyl butyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. At a concentration of 0.1%, the compound gave a wetting speed of 120 seconds and at a concentration of 0.25% a wetting speed of 40 seconds.

EXAMPLE 4

The salt of the amyl benzyl ester of chlorbenzoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing monochlorbenzene with maleic anhydride. The chlorbenzoyl acrylic acid thus formed was converted to its sodium salt and esterified with amyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 50 seconds at a concentration of 0.1% and a wetting speed of 19 seconds at a con centration of 0.25%.

EXAMPLE 5

The salt of the benzyl ester of toluoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing toluene with maleic anhydride. The toluoyl acrylic acid thus formed was converted to its sodium salt and esterified with benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 100 seconds at a concentration of 0.1% and a wetting speed of 20 seconds at a concentration of 0.25%.

EXAMPLE 6

The salt of the benzyl ester of ethyl benzoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing ethyl benzene with maleic anhydride. The resulting ethyl benzoyl acrylic acid was converted to its sodium salt and esterified with benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho compound. The compound gave a wetting speed of 60 seconds at a concentration of 0.2%.

EXAMPLE 7

The salt of the benzyl ester of sec-butyl chlorbenzoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing sec-butyl chlorbenzene with maleic anhydride. The resulting sec-butyl chlorbenzoyl acrylic acid thus formed was converted to its sodium salt and esterified with benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 25 seconds at a concentration of 0.1%.

EXAMPLE 8

The salt of the isopropyl benzyl ester of methyl benzoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing methyl benzene with maleic anhydride. The resulting methyl benzoyl acrylic acid was converted to its sodium salt and esterified with isopropyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 16 seconds at a concentration of 0.1%.

EXAMPLE 9

The salt of the methyl benzyl ester of sec-butyl benzoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing sec-butyl benzene with maleic anhydride. The sec-butyl benzoyl acrylic acid thus formed was converted to its sodium salt and esterified with methyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 15 seconds at a concentration of 0.1%.

EXAMPLE 10

The salt of the methyl benzyl ester of amyl benzoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing amyl benzene with maleic anhydride. The amyl benzoyl acrylic acid thus formed was converted to its sodium salt and esterified with methyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 11 seconds at a concentration of 0.1% and a wetting speed of 2 seconds at a concentration of 0.25%.

EXAMPLE 11

The salt of the amyl benzyl ester of toluoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing toluene with maleic anhydride. The toluoyl acrylic acid thus formed was converted to its sodium salt and esterified with amyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 25 seconds at a concentration of 0.1% and a wetting speed of 8 seconds at a concentration of 0.25%.

EXAMPLE 12

The salt of the isopropyl benzyl ester of isopropyl benzoyl (cumenoyl) sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing cumene with maleic anhydride. The cumenoyl acrylic acid thus formed was converted to its sodium salt and esterified with isopropyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 3 seconds at a concentration of 0.1%.

EXAMPLE 13

The salt of the isopropyl benzyl ester of sec-butyl benzoyl sulpho propionic acid was prepared following the procedure of Example 1, by first condensing sec-butyl benzene with maleic anhydride. The sec-butyl benzoyl acrylic acid thus formed was converted to its sodium salt and esterified with isopropyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 3 seconds at a concentration of 0.1%.

EXAMPLE 14

The salt of the sec-butyl benzyl ester of isopropyl benzoyl (cumenoyl) sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing cumene with maleic anhydride. The cumenoyl acrylic acid thus formed was converted to its sodium salt and esterified with sec-butyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 2 seconds at a concentration of 0.1%.

EXAMPLE 15

The salt of the sec-butyl benzyl ester of isopropyl toluoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing cymene with maleic anhydride. The cymenoyl acrylic acid thus formed was converted to its sodium salt and esterified with sec-butyl benzyl chloride, and the resulting ester with reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 2 seconds at a concentration of 0.1% and a wetting speed of "instantaneous" at a concentration of 0.25%.

EXAMPLE 16

The salt of the sec-butyl benzyl ester of sec-butyl benzoyl sulpho propionic acid with prepared, following the procedure of Example 1, by first condensing sec-butyl benzene with maleic anhydride. The sec-butyl benzoyl acrylic acid thus formed was converted to its sodium salt and esterified with sec-butyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 2 seconds at a concentration of 0.1%.

EXAMPLE 17

The salt of the diethyl benzyl ester of isopropyl benzoyl (cumenoyl) sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing cumene with maleic anhydride. The cumenoyl acrylic acid thus formed was converted to its sodium salt and esterified with diethyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 7 seconds at a concentration of 0.1%.

EXAMPLE 18

The salt of the diethyl benzyl ester of sec-butyl benzoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing sec-butyl benzene with maleic anhydride. The sec-butyl benzoyl acrylic acid thus formed was converted to its sodium salt and esterified with diethyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 4 seconds at a concentration of 0.1%.

EXAMPLE 19

The salt of the ethyl benzyl ester of sec-amyl benzoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing sec-amyl benzene with maleic anhydride. The sec-amyl benzoyl acrylic acid thus formed was converted to its sodium salt and esterified with ethyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 2 seconds at a concentration of 0.1%.

EXAMPLE 20

The salt of the benzyl ester of nonyl benzoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing nonyl benzene with maleic anhydride. The nonyl benzoyl acrylic acid thus formed was converted to its sodium salt and esterified with benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 35 seconds at a concentration of 0.1% and a wetting speed of 10 seconds at a concentration of 0.25%.

EXAMPLE 21

The salt of the sec-amyl benzyl ester of sec-butyl benzoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing sec-butyl benzene with maleic anhydride. The sec-butyl benzoyl acrylic acid thus formed was converted to its sodium salt and esterified with sec-amyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 17 seconds at a concentration of 0.1%.

EXAMPLE 22

The salt of the sec-butyl benzyl ester of sec-amyl benzoyl sulpho propionic acid was prepared, following the procedure of Example 1, by condensing sec-amyl benzene with maleic anhydride. The sec-amyl benzoyl acrylic acid thus formed was converted to its sodium salt and esterified with sec-butyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 6 seconds at a concentration of 0.1%.

EXAMPLE 23

The salt of the methyl benzyl ester of octyl toluoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing octyl toluene with maleic anhydride. The octyl toluoyl acrylic acid thus formed was converted to its sodium salt and esterified with methyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 35 seconds at a concentration of 0.1% and a wetting speed of 8 seconds at a concentration of 0.25%.

EXAMPLE 24

The salt of the benzyl ester of phenyl benzoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing phenyl benzene with maleic anhydride. The phenyl benzoyl sulpho propionic acid thus formed was converted to its sodium salt and esterified with benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 50 seconds at a concentration of 0.1%.

EXAMPLE 25

The salt of the butyl methyl benzyl ester of phenyl benzoyl sulpho propionc acid was prepared, following the procedure of Example 1, by first condensing phenyl benzene with maleic anhydride. The phenyl benzoyl acrylic acid thus formed was converted to its sodium salt and esterified with butyl methyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 12 seconds at a concentration of 0.1% and a wetting speed of 3 seconds at a concentration of 0.25%.

EXAMPLE 26

The salt of the benzyl ester of cyclohexyl benzoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing cyclohexyl benzene with maleic anhydride. The cyclohexyl benzoyl acrylic acid thus formed was converted to its sodium salt and esterified with benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 40 seconds at a concentration of 0.1%.

EXAMPLE 27

The amyl benzyl ester of cyclohexyl benzoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing cyclohexyl benzene with maleic anhydride. The cyclohexyl benzoyl acrylic acid thus formed was converted to its sodium salt and esterified with amyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 8 seconds at a concentration of 0.1% and a wetting speed of 2 seconds at a concentration of 0.25%.

EXAMPLE 28

The salt of the benzyl ester of chlornaphthoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing monochlornaphthalene with maleic anhydride. The chlornaphthoyl acrylic acid thus formed was converted to its sodium salt and esterified with benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 32 seconds at a concentration of 0.1% and a wetting speed of 11 seconds at a concentration of 0.25%.

EXAMPLE 29

The salt of the isopropyl benzyl ester of naphthoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing naphthalene with maleic anhydride. The naphthoyl acrylic acid thus formed was converted to its sodium salt and esterified with isopropyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 12 seconds at a concentration of 0.1%.

EXAMPLE 30

The salt of the methyl benzyl ester of methyl naphthoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing methyl naphthalene with maleic anhydride. The methyl naphthoyl acrylic acid thus formed was converted to its sodium salt and esterified with methyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 30 seconds at a concentration of 0.1%.

EXAMPLE 31

The salt of the propyl ethyl benzyl ester of methyl naphthoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing methyl naphthalene with maleic anhydride. The methyl naphthoyl acrylic acid thus formed was converted to its sodium salt and esterified with propyl ethyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 10 seconds at a concentration of 0.1% and a wetting speed of 3 seconds at a concentration of 0.25%.

EXAMPLE 32

The salt of the benzyl ester of tetrahydronaphthoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing tetrahydronaphthalene with maleic anhydride. The tetrahydronaphthoyl acrylic acid thus formed was converted to its sodium salt and esterified with benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 30 seconds at a concentration of 0.1% and a wetting speed of 8 seconds at a concentration of 0.25%.

EXAMPLE 33

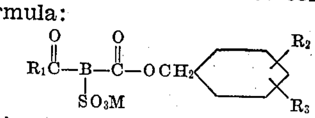
The salt of the sec-butyl benzyl ester of tetrahydronaphthoyl sulpho propionic acid was prepared, following the procedure of Example 1, by first condensing tetrahydronaphthalene with maleic anhydride. The tetrahydronaphthoyl acrylic acid thus formed was converted to its sodium salt and esterified with sec-butyl benzyl chloride, and the resulting ester was reacted with sodium bisulphite to form the sulpho derivative. The compound gave a wetting speed of 5 seconds at a concentration of 0.1%.

Of the foregoing compounds, the water-soluble salts of the butyl benzyl esters of the butyl benzoyl sulpho propionic acids and more specifically the sodium salt of the sec-butyl benzyl ester of sec-butyl benzoyl sulpho propionic acid; the water-soluble salts of the butyl benzyl esters of the propyl benzoyl sulpho propionic acids and more specifically the sodium salt of the sec-butyl benzyl esters of isopropyl benzoyl sulpho propionic acid; and the water-soluble salts of the propyl benzyl esters of the propyl benzoyl sulpho propionic acid and more specifically the sodium salt of the isopropyl benzyl ester of the isopropyl benzoyl sulpho propionic acid, are preferred.

Considerable modification is possible in the method of preparing the compounds as well as in selecting the various combinations of R_1, R_2, R_3, and M without departing from the scope of the invention.

I claim:

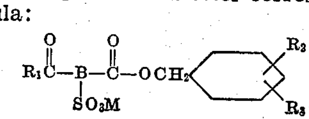
1. As a surface-active agent possessing marked wetting properties, a water-soluble salt of an aroyl sulpho propionic acid ester corresponding to the formula:



where R_1 is an aryl group selected from the group consisting of phenyl; monochlorophenyl; monoalkyl phenyl and monoalkyl monochlorophenyl, the alkyl groups of which contain from 1 to 9 carbon atoms; monoalkyl tolyl, the alkyl group of which contains from 1 to 8 carbon atoms; phenyl phenyl; phenyl chlorphenyl; cyclohexyl phenyl; cyclohexyl chlorphenyl; naphthyl; monochloronaphthyl; methyl naphthyl and tetrahydronaphthyl; where R_2 is selected from the group consisting of hydrogen and alkyl groups containing from 1 to 5 carbon atoms; where R_3 is selected from the group consisting of hydrogen and alkyl groups containing not more than 2 carbon atoms; the total number of carbon atoms in R_2 plus R_3 being no more than 5 and the total number of carbon atoms in R_2 plus R_3 plus any alkyl group on the aryl nucleus, R_1, being no more than 10, where B is an ethylene group, and wherein M is a cation providing water-solubility to the product.

2. The product of claim 1 wherein M is sodium.

3. As a surface-active agent possessing marked wetting properties, a water-soluble salt of a benzoyl sulpho propionic acid ester corresponding to the formula:



where R_1 is a monoalkyl phenyl group, the alkyl group of which contains from 1 to 5 carbon atoms; where R_2 is an alkyl group containing from 1 to 5 carbon atoms; where R_3 is hydrogen; where the total number of carbon atoms provided by R_2 and the alkyl group in R_1 is from 6 to 8; where B is an ethylene group, and where M is a cation providing water-solubility to the product.

4. The product of claim 3 wherein M is sodium.

5. The product of claim 3 wherein the alkyl group of R_1 contains 3 to 4 carbon atoms; wherein R_2 contains 3 to 4 carbon atoms, and wherein M is sodium.

6. As a surface-active agent possessing marked wetting properties, the sodium salt of a butyl benzyl ester of butyl benzoyl sulpho propionic acid.

7. As a surface-active agent possessing marked wetting properties, the sodium salt of the secondary butyl benzyl ester of secondary butyl benzoyl sulpho propionic acid.

8. As a surface-active agent possessing marked wetting properties, the sodium salt of a propyl benzyl ester of butyl benzoyl sulpho propionic acid.

9. As a surface-active agent possessing marked wetting properties, the sodium salt of the isopropyl benzyl ester of secondary butyl benzoyl sulpho propionic acid.

10. As a surface-active agent possessing marked wetting properties, the sodium salt of a butyl benzyl ester of propyl benzoyl sulpho propionic acid.

11. As a surface-active agent possessing marked wetting properties, the sodium salt of the secondary butyl benzyl ester of isopropyl benzoyl sulpho propionic acid.

12. The method of preparing a surface-active agent possessing marked wetting properties which comprises condensing in a Friedel-Crafts acylation reaction, an aryl derivative selected from the group consisting of benzene; monochlorobenzene; monoalkylbenzene and monoalkyl monochlorobenzene, the alkyl groups of which contain from 1 to 9 carbon atoms; monoalkyl toluene, the alkyl group of which contains from 1 to 8 carbon atoms; phenyl benzene; phenyl chlorbenzene; cyclohexylbenzene; cyclohexyl chlorbenzene; naphthalene; monochloronaphthalene; methyl naphthalene and tetrahydronaphthalene with maleic anhydride to form the corresponding aroyl acrylic acid, esterifying the resulting acid with an esterifying compound providing an ester group selected from the group consisting of benzyl; monoalkyl benzyl, the alkyl group of which contains from 1 to 5 carbon atoms; and dialkyl benzyl, the alkyl groups of which contain a total of not more than 5 carbon atoms, said esterifying compound being selected to provide an ester group which provides, along with any alkyl group attached to said aryl nucleus, a total number of carbon atoms in alkyl groups of no more than 10; and reacting the resulting ester with sodium bisulphite, at a temperature between about 80° C. and about 110° C., to form the sodium salt of the corresponding aroyl sulpho propionic acid ester.

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REFERENCES CITED

The following references are of record in the file of this patent:

Bogert et al.: J. A. C. S., vol. 47, pp. 526–535 (1925).