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SALTS OF (N-ALKYL-N-SULFOALKYLAMINO) ALKYL ALKYLATED PHENOLS

Van R. Gaertner, Dayton, Ohio, assignor to Monsanto Company, a corporation of Delaware

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This invention relates to aminoalkanesulfonate derivatives of alkylated phenols. In one respect, this invention relates to methods for solubilizing alkylated phenols by reaction with a reactive carbonyl compound and an aminoalkanesulfonate. In another respect, this invention relates to (N - alkyl - N - sulfoalkylamino)alkyl alkylated phenols as new compounds. In another respect, this invention relates to new surface active compositions. In another respect, this invention relates to new surfactant compositions which are highly resistant to curd-forming ingredients of hard water. In another respect, this invention relates to methods for increasing the lime soap dispersant, lathering and wetting efficiencies of detergent compositions.

It is generally well known that soaps, e.g., the sodium, potassium and ammonium salts of fatty acids precipitate as insoluble fatty acid salts, more commonly referred to as "lime soaps," in hard water or other water containing polyvalent metal ions such as calcium and magnesium ions. Such precipitated "lime soaps" have a tendency to coagulate and form undesirable curds, scums, films or deposits which are observed in the wash stand and bath tub and which stick to the clothes during the rinsing operation, thereby giving the clothes an unsightly, dingy appearance and a rancid odor. The formation of insoluble "lime soaps" also destroys or reduces the foaming and cleansing power of the soap.

Alkylated phenols are known to be fundamental hydrophobes for preparation of surfactants having good surface active properties, including wetting and foaming. However, the use of the alkylated phenols in soap and detergent compositions require that these compounds be solubilized by the attachment of a hydrophilic group to the molecule since the alkylated phenols are very insoluble in water. One method of solubilizing alkylated phenols involves reaction of the phenol with from 4 to 20 moles of ethylene oxide. Another method of solubilizing phenols involves sulfonation of the alkylated phenol by treatment with sulfuric acid or sulfur trioxide.

An object of this invention is to provide a method for solubilizing alkylated phenols by reaction with a reactive carbonyl compound and an N-alkylaminoalkanesulfonic acid salt.

Another object of this invention is to provide salts of (N-alkyl-N-sulfoalkylamino)alkyl alkylated phenols as new compounds.

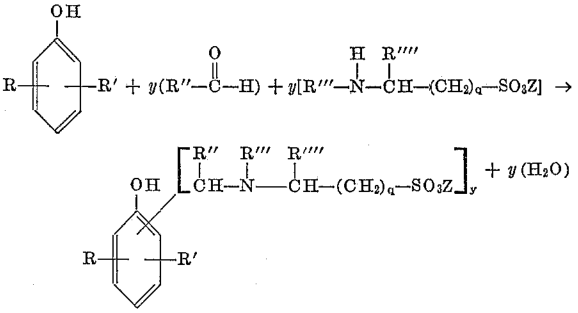
Another object of this invention is to provide new surface-active compositions having high foaming and wetting efficiencies.

Another object of this invention is to provide new all-purpose soap compositions which form little or no insoluble lime soap curd when used with hard water.

Another object of this invention is to provide a method for increasing the lime soap dispersant efficiency of soap-containing detergent compositions to reduce the coagulation of precipitated lime soap in hard water and thereby prevent the formation of curds, scums, deposits, films, and the like.

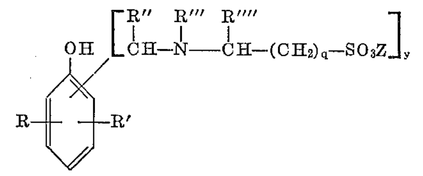
Other aspects, objects and advantages of this invention will be apparent from the consideration of the accompanying disclosure and the appended claims.

In accordance with the present invention, an alkylated phenol is reacted with an aldehyde and an N-alkylaminoalkanesulfonate salt to solubilize said alkylated phenol and form a salt of an (N-alkyl-N-sulfoalkylamino)alkyl alkylated phenol. The reaction can be illustrated by the following equation:



wherein R is an alkyl radical of from 1 to 20 carbon atoms; R′ is selected from the group consisting of hydrogen and alkyl radicals of from 1 to 20 carbon atoms, the total number of carbon atoms of said R and said R′ always being greater than 8 and less than 20 carbon atoms, either the same or different; R″ is selected from the group consisting of hydrogen and alkyl radicals of from 1 to 3 carbon atoms; R‴ is an alkyl radical of from 1 to 4 carbon atoms; R⁗ is selected from the group consisting of hydrogen and alkyl radicals of 1 and 2 carbon atoms; *q* is an integer selected from the group consisting of 2, 3, and 4 when R⁗ is hydrogen, *q* is an integer selected from the group consisting of 1 and 2 when R⁗ is an alkyl radical of 1 carbon atom, and *q* is an integer of 1 when R⁗ is an alkyl radical of 2 carbon atoms; Z is a salt forming group selected from the group consisting of alkali metal, alkaline earth metal, and ammonia; and *y* is an integer selected from the group consisting of 1, 2, and 3 when R and R′ are meta alkyl radicals, *y* is an integer selected from the group consisting of 1 and 2 when R′ is an ortho alkyl radical, *y* is an integer selected from the group consisting of 1 and 2 when R′ is a para alkyl radical, and *y* is an integer of 1 when R and R′ are ortho and para radicals.

Also, according to the present invention, there are provided, as new compounds, substituted alkylated phenols of the formula



wherein R, R′, R″, R‴, R⁗, *q*, Z and *y* are as above defined.

Further, according to the present invention, there are provided new surface-active compositions comprising, as the active ingredient, a (N-alkyl-N-sulfoalkylamino)alkyl alkylated phenol of the formula given above.

Further, according to the present invention, there are provided new all-purpose detergent compositions comprising a sodium, potassium or ammonium salt of a long-chain fatty acid and, as an essential ingredient, an (N-alkyl-N-sulfoalkylamino)alkyl alkylated phenol of the formula given above.

Further, according to the invention, there are provided methods for increasing the lime soap disperant efficiency of soap-containing detergent compositions by adding an (N-alkyl-N-sulfoalkylamino)alkyl alkylated phenol of the formula given above to a soduim, potassium or ammonium long-chain fatty acid soap.

The alkylated phenols used in the reaction of the present invention can be either mono- or dialkylated with alkyl groups containing from 1 to 20 carbon atoms of either straight-chain or branched-chain configuration. In the mono-alkylated phenols, the length of the carbon chain of the alkyl radical is always greater than 8 carbon atoms. In the dialkylated phenols, the total number of carbon atoms in the two alkyl radicals is always less than 20 carbon atoms and greater than 8 carbon atoms. These alkyl radicals are attached to the benzene ring of the phenol predominantly in positions which are ortho or para to the hydroxy group. Thus, alkyl radicals can be attached to the benzene ring in meta positions and also other non-reactive groups, such as halogen, can be attached in these same positions. Methods for producing alkylated phenols are well known to those skilled in the art, such as by alkylating phenol in the presence of an acid catalyst with polyisobutylene or tri- and/or tetra-propylene.

Illustrative examples of some alkylated phenols which can be employed as reactants in this invention include the following: 2- or 4-nonylphenol; 2- or 4-dodecylphenol; 2- or 4-pentadecylphenol; 2- or 4-heptadecylphenol; 2-methyl-6-octylphenol; 2-methyl-4-octylphenol; 2-octyl-4-methylphenol; 2-octyl-6-propylphenol; 2,6-dioctylphenol; 2,6-diamylphenol; 2,6-di-sec-amylphenol; 2,6 - dinonylphenol; 2,6-bis(2-methyl-2-pentyl)phenol; 2,4-di-sec-amylphenol; 2,4-bis(2-hexyl)phenol; 2,4-bis(4-methyl-2-pentyl)phenol; 2,4-bis(2-methyl-2-butyl)phenol.

The aldehyde reactant used in the reaction of this invention can be any aldehyde containing not more than 4 carbon atoms. Illustrative examples of some aldehydes which can be used include the following: formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, and iso-butyraldehyde.

The N-alkylaminoalkanesulfonate reactants used in the reaction of this invention must contain at least 2 carbon atoms in the alkane group and, preferably, fewer than 4 carbon atoms. The alkyl radicals substituted on the nitrogen atom can contain from 1 to 4 carbon atoms, such as methyl, ethyl, propyl and butyl radicals. The aminoalkanesulfonate reactant must be in the form of a salt, substantially free of unneutralized sulfonic acid, because the reaction of this invention will not take place if the N-alkylaminoalkanesulfonate reactant is replaced by a corresponding sulfonic acid. The salt forming group of the aminoalkanesulfonate can be either an alkali metal, an alkaline earth metal, or ammonium. The alkali metal can be selected from the group consisting of sodium, potassium and lithium and the alkaline earth metal can be selected from the group consisting of calcium, strontium, barium and magnesium.

Illustrative examples of some N-alkylaminoalkanesulfonate reactants which can be employed in this invention include the following: sodium N-methyl-2-aminoethanesulfonate or sodium N-methyl-taurate, sodium N-ethyl-2-aminoethanesulfonate, potassium N-methyl-2-aminoethanesulfonate, potassium N-propyl - 2 - aminoethanesulfonate, sodium N-methyl-3-aminopropanesulfonate, lithium N-butyl-3-aminopropanesulfonate, sodium N-ethyl-4-aminobutanesulfonate, barium N-isopropyl-4-aminobutanesulfonate, calcium N-ethyl-2-aminoethanesulfonate, calcium N-propyl - 4 - aminobutanesulfonate, strontium N-methyl-3-aminopropanesulfonate, ammonium N-methyl-2-aminoethanesulfonate, ammonium N-isobutyl-3-aminopropanesulfonate, sodium-N-methyl-2-aminobutanesulfonate, sodium N-ethyl-3-aminobutanesulfonate, and soduim N-methyl-2-aminopropanesulfonate.

Although the reaction of this invention proceeds very readily, and can be accomplished at room temperature merely by bringing the reactants together, it is generally preferred to use an elevated temperature in order to obtain shorter reaction times and higher yields. Ordinarily, a temperature below 125° C. is employed and preferably the temperature is within the range of from 30° C. to 100° C. At temperatures much higher than 125° C., there is a tendency for the aminoalkanesulfonate salt to decompose; however, somewhat higher temperatures can be used provided super-atmospheric pressure is employed. Thus, the reaction is ordinarily conducted at atmospheric pressure but sub-atmospheric and super-atmospheric pressures can also be used. Preferably, the reaction is carried out in a solvent medium in which the alkylated phenol reactant is dissolved or suspended. Although the reaction can be carried out using water as the solvent, preferably a water-soluble solvent in which the alkylated phenol is soluble is used because the alkylated phenol is not soluble in pure water. Examples of some water-soluble solvents which can be used include methyl alcohol, ethyl alcohol, and dioxane. These solvents can be used in admixture with water if desired.

The alkylated phenol, aldehyde and aminoalkanesulfonate reactants can be reacted together in any order provided the alkylated phenol is the last added reactant. Preferably, the aldehyde and the aminoalkanesulfonate reactants are admixed together and the alkylated phenol reactant is then added to the reaction mixture. The reactants are usually employed in equimolar proportions when it is desirable to substitute one N-alkyl-sulfoalkylaminoalkyl group on the benzene ring of the alkyl phenol.

The reaction product, i.e., the salt of an (N-alkyl-N-sulfoalkylaminoalkyl)alkylphenol, is separated from the reaction mixture by simply removing any unreacted constituents, e.g., by distillation, decantation, extraction or other means well known to the art and then drying the product. The salts of (N-alkyl-N-sulfoalkylaminoalkyl)-alkylphenols prepared by the present process are usually white, waxy to crystalline solids. Generally, the reaction product produced comprises a mixture of phenols which are both mono and di-substituted with the solubilizing group, except when the phenol is a dialkylated one in which case the reaction product is only mono-substituted with this solubilizing group. However, reaction products wherein a mono-alkylphenol is substituted with two solubilizing groups are also obtained in high yield. Illustrative examples of some specific phenol products produced by the reaction of this invention are as follows:

sodium 2-[N-methyl-N-(2-sulfoethyl)aminomethyl]-6-nonylphenol;
potassium 2-[N-ethyl-N-(2-sulfoethyl)aminomethyl]-4-dodecylphenol;
ammonium 4-[N-butyl-N-(3-sulfopropyl)aminomethyl]-2-pentadecylphenol;
calcium 2-[N-ethyl-N-(2-sulfoethyl)-1-aminoethyl]-6-nonylphenol;
barium 2-[N-butyl-N-(3-sulfopropyl)-1-aminopropyl]-6-dodecylphenol;
sodium 2-[N-methyl-N-(2-sulfoethyl)aminomethyl]-4,6-dinonylphenol;
sodium 2-[N-methyl-N-(2-sulfoethyl)aminomethyl]-4,6-di-sec-amylphenol;
sodium 4-[N-methyl-N-(2-sulfoethyl)aminomethyl]-2-methyl-6-octylphenol;
sodium 2-[N-methyl-N-(2-sulfoethyl)aminomethyl]-4,6-bis(2-methyl-2-pentyl)phenol;
potassium 2-[N-butyl-N-(2-sulfoethyl)-1-aminopropyl]-4-nonylphenol;
potassium 4-[N-ethyl-N-(3-sulfopropyl)aminomethyl]-2,6-diamylphenol;
lithium 2-[N-butyl-N-(2-sulfoethyl)-1-aminopropyl]-4-pentadecylphenol;
calcium 4-[N-butyl-N-(3-sulfopropyl)aminomethyl]-2-ethyl-6-octylphenol;
calcium 2-[N-propyl-N-(2-sulfoethyl)-1-aminobutyl]-4-heptadecylphenol;
barium 4-[N-methyl-N-(4-sulfobutyl)-1-aminopropyl]-2-methyl-6-dodecylphenol;
disodium 4-dodecyl-2,6-bis[N-methyl-N-(2-sulfoethyl)-aminomethyl]phenol;
dipotassium 4-pentadecyl-2,6-bis[N-propyl-N-(2-sulfoethyl)-1-aminoethyl]phenol;

disodium 2-heptadecyl-4,6-bis[N-ethyl-N-(3-sulfopropyl)aminomethyl]phenol;
diammonium 4-nonyl-2,6-bis[N-butyl-N-(2-sulfoethyl)-1-aminopropyl]phenol;
dilithium 2-tridecyl-4,6-bis[N-methyl-N-(3-sulfopropyl)-1-aminobutyl]phenol;
calcium 4-hexadecyl-2,6-bis[N-ethyl-N-(2-sulfoethyl)-1-aminoethyl]phenol; and
barium 2-dodecyl-4,6-bis[N-methyl-N-(4-sulfobutyl)-aminomethyl]phenol.

The advantages,the desirability and usefulness of the present invention will be illustrated by the following examples.

Example 1

In this example, sodium N-methyl-N-(2-sulfoethyl) aminomethyl-nonylphenol and disodium bis[N-methyl-N-(2-sulfoethyl)aminomethyl]-nonyl phenol were produced in a ratio of mono- to di-substitution products of 34:66. A mixture containing 22.0 g. of nonylphenol (0.10 mole), 65 g. of a 35% solution of N-methyltaurine, sodium salt, (0.12 mole), 50 ml. of ethyl alcohol and 50 ml. of water was formed. While maintaining this mixture at a temperature of 25° C., 12.2 g. of a 37% formaldehyde solution (0.15 mole) was added with stirring. The reaction mixture was heated during a period of 30 minutes to a temperature of 80° C. and maintained at a temperature in the range of 75° C. to 80° C. for a period of one hour. After allowing the resulting mixture to cool, 300 ml. of isopropyl alcohol was added to precipitate a gummy material. The resulting mixture of liquor and the precipitated solids was evaporated under vacuum at a temperature of approximately 60° C. to near dryness and the residue dissolved in 400 ml. of methanol. The insoluble salts present in the methanol solution were removed by filtration and 300 ml. of isopropanol was added slowly to the filtrate to precipitate the sodium N-methyl-N-(2-sulfoethyl)aminomethylnonylphenol and disodium bis[N - methyl - N - (2 - sulfoethyl)aminomethyl]nonylphenol as crystalline solids, which were separated from the liquor by filtration and washed with isopropanol before being dried under vacuum at a temperature of 45° C.

Example 2

In this example, sodium N-methyl-N-(2-sulfoethyl)-aminomethyldinonylphenol was prepared. A 2-component reactant solution was first prepared from 460 g. of 35% N-methyltaurine sodium salt and 81 g. of 37% formaldehyde together with sufficient water to obtain a total volume of 500 ml. of solution. To a 60 ml. portion of this solution (containing 0.12 mole of each of these reactants) and 60 ml. of ethanol was added 34.7 g. of dinonylphenol (0.10 mole) at an initial reaction temperature of 35° C. The temperature of the reaction mixture was increased by heating to 81° C. in a period of one hour and fifty minutes and this temperature was maintained with continuous stirring for a period of an additional eight hours. The reaction mixture formed was cooled and the small amount of insoluble precipitate present was dissolved by the addition of hot water. The resulting solution was washed with 200 ml. hexane to form two phases. The hexane-containing phase was separated and extracted with two separate 200 ml. portions of methanol to form two phases. The methanol containing phases were combined and distilled at slightly elevated temperature under vacuum with the periodic introduction of isopropanol to remove water and volatile materials and leave the product dissolved in the isopropanol. The insoluble salts which separated from the isopropanol solution were removed by filtration and then the isopropanol solution was evaporated under vacuum to dryness to form 49.5 g. of sodium N-methyl-N-(2-sulfoethyl)aminomethyldinonylphenol which is a cream color brittle gum. This compound analyzed 9.52% hydrogen, 3.00% nitrogen, and 6.71% sulfur as compared with calculated values of 9.70% hydrogen, 2.69% nitrogen, and 6.17% sulfur for $C_{28}H_{50}NNaO_4S$.

Example 3

Sodium N-methyl-N-(2-sulfoethyl)aminomethyl-di-sec-amyl phenol was prepared in this example from 23.4 g. of di-sec-amyl phenol (0.10 mole) and 60 ml. of the reagent solution prepared in Example 2 containing 0.12 mole each of formaldehyde and N-methyltaurine sodium salt. The di-sec-amyl phenol was added slowly with stirring to a mixture of the reagent solution to which had been added 60 ml. of ethanol. The initial temperature of 35° C. of the reaction mixture was increased to 82° C. in a period of 1.5 hours and this latter temperature was maintained for a period of one hour with continuous stirring. The reaction mixture obtained was concentrated by evaporation under vacuum and water removed by distillation under vacuum and at slightly elevated temperature with the periodic introduction of ethanol. The insoluble salts which precipitated out of the resulting ethanol solution were separated by filtration and the filtrate was evaporated to dryness at a temperature of less than 100° C. and a pressure less than 40 mm. to obtain 42.6 g. of sodium N-methyl-N-(2-sulfoethyl)aminomethyl-di-sec-amylphenol. This product had a nitrogen content of 4.15% as compared with 3.44% calculated for $C_{20}H_{34}O_4NNaS$.

Example 4

In this example, sodium N-methyl-N-(2-sulfoethyl)-aminomethyldiamylphenol was prepared from 23.4 g. of diamylphenol (0.10 mole) and 60 ml. of the reagent solution of Example 1 containing 0.12 mole of formaldehyde and N-methyltaurine sodium salt. The reagent solution and 60 ml. of ethanol were mixed together and the diamylphenol added slowly with stirring. The temperature of the reaction mixture was increased to 80° C. in a period of 10 minutes and the reaction mixture was maintained at this temperature for a period of four hours and fifteen minutes. The resulting reaction mixture was distilled under vacuum at slightly elevated temperature with the periodic introduction of isopropanol to remove water and volatile materials. The colored solution in isopropanol was decolorized and freed of insoluble salts by filtration through charcoal using methanol to wash the filter cake. The recovered filtrate was concentrated by heating under vacuum to remove methanol and leave the product in the isopropanol solution. Upon cooling, the product crystallized and was recovered by filtration. The recovered solid material was dried in an oven at 50° C. to yield 16.0 g. of sodium N-methyl-N-(2-sulfoethyl)aminomethyldiamylphenol. The recovered filtrate was concentrated, cooled and filtered to recover another 8.0 g. of the product.

Example 5

In this example, sodium N-methyl-N-(2-sulfoethyl)-aminomethylmethyloctylphenol was prepared from 20.8 g. of octylcresol (0.10 mole) and 60 ml. of the reagent solution of Example 2 containing 0.12 mole of each of formaldehyde and N-methyltaurine sodium salt. The formaldehyde and N-methyltaurine sodium salt reagent solution was admixed with 60 ml. of ethanol to which the octylcresol was added slowly with stirring. The reaction mixture was heated for a period of 1.5 hours with continuous stirring while maintaining the temperature at 81° C. The resulting reaction mixture was then distilled at a slightly elevated temperature under vacuum with the periodic introduction of isopropanol to remove water and volatile materials, including ethanol. The salts precipitating out of the resulting hot isopropanol solution were removed by filtration through charcoal to which had been added filter aid. The filter cake was washed with hot methanol and the total filtrate was distilled to remove the methanol. The product was permitted to crystallize out of solution by cooling the resulting isopropanol solution and removed therefrom by filtration to recover 21.0 g. of sodium N-methyl-N-(2-sulfoethyl)-aminomethylmethyloctylphenol as an off-white powdery solid.

Example 6

In this example, disodium dodecyl-bis[N-methyl-N-(2-sulfoethyl)aminomethyl]phenol was prepared from 26.2 2. of dodecylphenol (0.10 mole) and 105 ml. of the reagent solution of Example 2 containing 0.25 mole each of formaldehyde and N-methyltaurine sodium salt. The dodecylphenol was added slowly with stirring to the reaction solution to which had also been added 100 ml. of ethanol. The reaction mixture was maintained at a temperature of 82° C. for a period of 2.5 hours with continuous stirring. At the end of this time, the reaction mixture was distilled at a slightly elevated temperature under vacuum with the periodic introduction of isopropanol to remove water and volatile materials The resulting isopropanol solution was diluted with isopropanal to form a total volume of 30 ml. One hundred milliliters of methanol was added to the isopropanol solution to dissolve the product completely. The white precipitate present in the solution was removed by filtration and washed with methanol. The total filtrate was evaporated to dryness at a temperature of 100° C. under vacuum to form 52.4 g. of disodium dodecyl-bis[N-methyl-N-(2-sulfoethyl)aminomethyl]phenol which is a tough resinous gum having a light cream color. An analysis of this product showed 7.42% hydrogen, 4.57% nitrogen, and 10.52% sulfur which compared with 7.60% hydrogen, 4.60% nitrogen and 10.52% sulfur calculated for $C_{26}H_{46}N_2Na_2S_2O_7$.

Example 7

Sodium N-methyl - N - (2-sulfoethyl)aminomethyl-2-methylnonylphenol was prepared from 35.2 g. of nonyl-o-cresol (0.15 mol) and 85 ml. of the reagent solution of Example 2 containing 0.17 mole each of formaldehyde and N-methyltaurine sodium salt. The nonyl-o-cresol was added to the reagent solution to which had been added 85 ml. of ethanol and heated with continuous stirring at a temperature of 81° C. for a period of 6.5 hours. At the end of this time, the precipitated solids present in the reaction mixture were removed by filtration. The recovered filtrate was treated with 100 ml. of hexane and 50 ml. of water to form two phases. The hexane-containing upper layer was separated and treated with methanol again to form two phases. Both lower layers were combined and distilled at slightly elevated temperature under vacuum with the periodic introduction of isopropanol to remove water and volatile materials. The resulting isopropanol solution containing the product was then evaporated to dryness to recover 60.0 g. of sodium N-methyl - N - (2-sulfoethyl)aminomethyl-2-methylnonlyphenol, which is a gummy material. This product analyzed 8.5% hydrogen, 3.48% nitrogen and 7.5% sulfur as compared with calculated values of 8.41% hydrogen, 3.44% nitrogen and 7.8% sulfur.

Example 8

In this example, sodium N-methyl-N-(2-sulfoethyl)-aminomethyl-di-2-hexylphenol was prepared from 26.2 g. of di-sec-hexylphenol (0.10 mole) and 60 ml. of the reagent solution of Example 2 containing 0.12 mole each of the formaldehyde and the N-methyltaurine sodium salt reactants. The reagent solution was first mixed with 60 ml. of ethanol and then the di-sec-hexylphenol was added slowly with stirring. The reaction mixture was then heated at a temperature of 79° C. with continuous stirring for a period of two hours and twenty minutes. At the end of this time, the reaction mixture was cooled and the insoluble salts present removed by filtration. The recovered filtrate was distilled at slightly elevated temperature under vacuum with the periodic introduction of isopropanol to remove water and other volatile materials. The isopropanol solution was then aspirated to dryness at a temperature of 100° C. to give 47.3 g. of the product which was further dried in an oven under vacuum at a temperature of 60° C. to yield 46.0 g. of sodium N-methyl - N - (2-sulfoethyl)aminomethyl - di-2-hexylphenol which is a somewhat brittle material. The nitrogen analysis of this product was 3.95% as compared with a value of 3.25% calculated for $C_{22}H_{34}NNaO_4S$.

Example 9

In this example, sodium N-methyl-N-(2-sulfoethyl) aminomethyl-di(4-methyl-2-pentyl)phenol was prepared from 23.4 g. of di(4-methyl-2-pentyl)phenol and 60 ml. of the reagent solution of Example 2 containing 0.12 mole each of formaldehyde and N-methyltaurine sodium salt. The reagent solution was first mixed with 60 ml. of ethanol and then the di(4-methyl-2-pentyl)phenol was added slowly with stirring. The reaction mixture was then heated at a temperature of 82° C. for a period of four hours. At the end of this time, the insoluble salts present in the reaction mixture were removed by filtration and the filtrate was distilled at slightly elevated temperature under vacuum with the periodic introduction of isopropanol to remove water and other volatile meterials. The resulting isopropanol solution was diluted with additional isopropanol to give a total volume of 700 ml. The insoluble materials present in the resulting solution were removed by filtration at an elevated temperature. The recovered filtrate was cooled overnight with the formation of a very flocculent precipitate which was then recovered by filtration and dried in an oven at a temperature of 60° C. under vacuum to yield 30.1 g. of sodium N-methyl-N-(2-sulfoethyl) aminomethyl-di-(4-methyl-2-pentyl)phenol which is a very powdery crystalline material.

Example 10

In this example, 35.0 g. of di(2-methyl-2-butyl)phenol (0.15 mole) was reacted with 51 g. of the reagent solution of Example 2 containing 0.155 mole each of formaldehyde and N-methyltaurine sodium salt. The reagent solution was first mixed with 50 ml. of ethanol and then the phenol reactant was added slowly with stirring. After the addition of the phenol, the reaction mixture was heated at a temperature of 82° C. for a period of five hours, and then distilled under slightly elevated temperature and vacuum with the periodic introduction of isopropanol to remove water and volatile materials. The hot isopropanol solution recovered contained a large amount of a precipitated material which was found to be an isomer of the product. This precipitated material was removed by filtration from the hot isopropanol solution and dried at a temperature of 60° C. under vacuum to yield 22.5 g. of an isomer of sodium N-methyl-N-(2-sulfoethyl)aminomethyl-di-(2-methyl-2-butyl)phenol which is herein identified as isomer A. The filtrate recovered from the previous separation step was cooled to crystallize out a product which was removed by filtration and dried at a temperature of 60° C. under vacuum to yield 29.0 g. of a second isomer of sodium N-methyl-N-(2-sulfoethyl)aminomethyl-di-(2-methyl-2-butyl)phenol which is herein identified as isomer B.

Example 11

The wetting efficiencies of a number of the compounds of this invention were determined by the Draves Wetting Test of the American Association of Textile Chemists.

The following wetting times were measured at the concentrations shown:

Compound	Time in Seconds					
	0.5%	0.25%	0.125%	0.062%	0.031%	0.015%
Product of Example 1	3.0	6.6	29.9	108.4	+180	--------
Product of Example 3	2.4	4.3	10.0	36.7	+180	--------
Product of Example 4	[1] Inst.	2.4	5.7	--------	--------	--------
Product of Example 5	2.4	5.5	20.0	150.7	--------	--------
Product of Example 6	12.6	19.6	53.1	+180	--------	--------
Product of Example 7	10.8	16.1	45.7	65.9	+180	--------
Product of Example 8	31.9	52.7	134.0	+180	--------	--------
Product of Example 9	8.1	8.1	13.1	24.1	66.9	+180
Product of Example 10 (Isomer A)	[1] Inst.	2.7	5.2	13.7	146.9	+180
Product of Example 10 (Isomer B)	[1] Inst.	2.1	4.4	7.4	32.0	165.5

[1] Inst.—instantaneous.

Example 12

A number of the new compounds of this invention were evaluated with respect to lathering activity as determined by the Ross-Miles Lathering Test of the American Society for Testing Materials. In the following results, the lather height is measured in centimeters in water of 50 p.p.m and 300 p.p.m. hardness.

Compound	50 p.p.m. hardness at once/ 5 mins.	300 p.p.m. hardness at once/ 5 mins.
Product of Example 1	16.0/16.0	19.5/19.4
Product of Example 2	12.5/12.3	----------
Product of Example 3	14.8/2.0	17.0/6.8
Product of Example 4	18.1/8.8	19.1/18.8
Product of Example 5	----------	13.3/11.7
Product of Example 6	18.6/18.0	13.6/13.6
Product of Example 7	16.3/13.9	----------
Product of Example 8	16.0/15.3	----------
Product of Example 9	20.7/20.7	----------
Product of Example 10 (Isomer A)	----------	18.4/17.6
Product of Example 10 (Isomer B)	----------	18.6/8.2

Example 13

In this example, the lime soap dispersion efficiency of a number of the new compounds of this invention were determined using the method described by. J. C. Harris in ASTM Bulletin No. 140, 00. 1–13, May 1946. These results are reported in the table below wherein the dispersion number is equal to 10 times the milliliters of the test compound required to disperse 45.5 mg. of calcium oleate formed.

Compound:	Dispersion number
Product of Example 1	80.
Product of Example 2	Greater than 80.
Product of Example 3	20.
Product of Example 4	20.
Product of Example 5	40.
Product of Example 6	40.
Product of Example 7	40.
Product of Example 8	Greater than 80.
Product of Example 9	60.
Product of Example 10 (Isomer A)	40.
Product of Example 10 (Isomer B)	20.

Example 14

In this example, the lime soap dispersion of the compounds of Examples 3 and 4 and was determined in secondary tests using the Terg-o-tometer test. In this test, the formation of soap curds is observed visually and compared with the soap curd formation of known lime soap dispersants. One hundred milliliters of a soap solution containing 0.32% Rinso, 100 ml. of a dispersant solution containing 0.061% of the candidate dispersant, and 800 ml. of 180 p.p.m. hard water, all at a temperature of 115° F., were admixed together and agitated for a period of 20 minutes, followed by visual inspection of the resulting mixture in a 100-ml. beaker. In the sample in which no dispersant is used, 100 ml. of the soap solution is mixed with 900 ml. of the 180 p.p.m. hard water. In this test, sodium N-methyl-N-(2-sulfoethyl)-aminomethyl-di-sec-amylphenol and sodium N-methyl-N-(2-sulfoethyl)aminomethyl-di-amylphenol each had a rating of 2 which is equivalent to the rating of a well known commercial lime soap dispersant, Igepon TE-42.

The salts of (N-alkyl-N-sulfoalkylaminoalkyl)alkylated phenols produced by the process of this invention are valuable articles of commercial interest and have many varied uses, particularly as surface active agents. They can be used as wetting, frothing, or washing agents in the treating and processing of textiles, for dying, for the pasting of dye-stuffs, for fulling, sizing, impregnating and bleaching, and the like. In addition, these compounds are useful for preparing foam in fire extinguishers, for use as froth flotation agents, as air-entraining agents for concrete or cement, and as aids in the preparation of other articles of commerce. These compounds are particularly useful in soap and synthetic detergent compositions.

As surface active compositions, the salts of the (N-alkyl-N-sulfoalkylaminoalkyl)alkylated phenols of this invention comprise either the pure compounds or an admixture of the pure compound with an adjuvant material or a diluent. Ordinarily, the compounds of this invention are employed in surface active applications in a diluted form wherein the compound is dissolved or suspended in some liquid medium such as water or methyl alcohol. The compounds of this invention can also be admixed with adjuvant materials, particularly when used in soap or synthetic detergent compositions, such as common inorganic builders of the type of carbonates, phosphates, silicates and fillers such as starch.

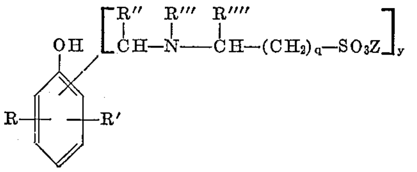
The new alkylated phenols of this invention are particularly useful in soap and synthetic detergent compositions because these compounds possess unusually high "lime soap" dispersion properties. The relative proportions of the alkylated phenols of this invention and the soap and/or synthetic detergent in the new compositions may vary greatly, depending upon the use intended for the composition. Although useful solubilizing wetting and lathering compositions of high detergency can be formed by mixing small proportions of soap with large proportions of the salts of (N-alkyl-N-sulfoalkylamino-alkyl)alkylated phenols, usually the greatest value of soap compositions of the present invention lie in compositions having less than 75% by weight of the alkylated phenol. In general, it is preferred to incorporate in the soap composition about 5 to 50% by weight of the salt of the (N-alkyl-N-sulfoalkylaminoalkyl)alkylated phenol based upon the total weight of the soap and the alkylated phenol. Of course, other materials such as perfumes, fillers, and inorganic builders of the type such as carbonates, phosphates and silicates, can also be present in the composition.

The soaps which are useful in the novel compositions of this invention are the so-called water soluble soaps of the soap-making art and include sodium, potassium, ammonium and amine salts of the higher fatty acids, that is, those having about 8 to about 20 carbon atoms per molecule. These soaps are normally prepared from such naturally-occurring esters as cocoanut oil, palm oil, olive oil, cottonseed oil, tung oil, corn oil, castor oil, soybean oil, wood fat, tallow, whale oil, menhaden oil, and the like, as well as mixtures of these.

Reasonable variation and modification are possible within the scope of the foregoing disclosure and the appended claims of this invention the essence of which is that there have been provided (1) methods for reacting an alkylated phenol with an aldehyde and an N-alkyl aminoalkanesulfonate salt to solubilize said alkylated phenol and form a salt of an (N-alkyl-N-sulfoalkylamino)alkyl alkylated phenol, (2) said (N-alkyl-N-sulfoalkylamino)alkyl alkylated phenols as new compounds, (3) said (N-alkyl-N-sulfoalkylamino)alkyl alkylated phenols as new surface active compositions, (4) a new all-purpose detergent composition comprising a sodium, potassium, or ammonium long-chain fatty acid soap and said (N-alkyl-N-sulfoalkylamino)alkyl alkylated phenol, and (5) methods for increasing the lime soap dispersion efficiency of soap-containing detergent compositions by incorporating an (N-alkyl-N-sulfoalkylamino)alkyl alkylated phenol therein.

I claim:

1. An organic compound of the formula



wherein R is an alkyl radical of from 1 to 20 carbon atoms; R′ is selected from the group consisting of hydrogen and alkyl radicals of from 1 to 20 carbon atoms, the sum total number of carbon atoms of said R and R′ always being greater than 8 and less than 20 carbon atoms, R″ is selected from the group consisting of hydrogen and alkyl radicals of from 1 to 3 carbon atoms; R‴ is an alkyl radical of from 1 to 4 carbon atoms; R⁗ is selected from the group consisting of hydrogen and alkyl radicals of 1 and 2 carbon atoms; *q* is an integer selected from the group consisting of 2, 3, and 4 when R⁗ is hydrogen, *q* is an integer selected from the group consisting of 1 and 2 when R⁗ is an alkyl radical of 1 carbon atom, and *q* is an integer of 1 when R⁗ is an alkyl radical of 2 carbon atoms; Z is a salt-forming group selected from the group consisting of alkali metal, alkaline earth metal and ammonium; and *y* is an integer selected from the group consisting of 1, 2, and 3 when R and R′ are meta alkyl radicals, *y* is an integer selected from the group consisting of 1 and 2 when R′ is an ortho alkyl radical, *y* is an integer selected from the group consisting of 1 and 2 when R′ is a para alkyl radical, and *y* is an integer of 1 when R and R′ are ortho and para radicals; wherein the amino methyl sulfonate groups are substituted in positions ortho and para to the phenolic hydroxyl group.

2. Sodium N-methyl-N-(2-sulfoethyl)aminomethylnonylphenol.

3. Sodium N-methyl-N-(2-sulfoethyl)aminomethyldinonylphenol.

4. Sodium N-methyl-N-(2-sulfoethyl)aminomethyl-di-sec-amylphenol.

5. Sodium N-methyl-N-(2-sulfoethyl)aminomethyldiamylphenol.

6. Sodium N-methyl-N-(2-sulfoethyl)aminomethylmethyloctylphenol.

7. Sodium dodecyl-bis[N-methyl-N-(2-sulfoethyl)-aminomethyl]phenol.

8. Sodium N-methyl-N-(2-sulfoethyl)aminomethyl-di-2-hexylphenol.

References Cited by the Examiner

UNITED STATES PATENTS

2,319,078	5/1943	McNally et al.	260—509
2,678,333	5/1954	Hartough et al.	260—509
2,774,735	12/1956	Becher	252—117
2,803,652	8/1957	Riat	260—509
2,861,955	11/1958	Aylesworth	252—117

OTHER REFERENCES

Burckhalter et al.: J. Am. Chem. Soc., vol. 68, 1946, p. 1894, 1897 relied upon.

Schwartz et al.: "Surface Active Agents," 1949 (pages 102–103).

LORRAINE A. WEINBERGER, *Primary Examiner.*

JULIUS GREENWALD, CHARLES B. PARKER, LEON ZITVER, *Examiners.*