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3,072,690

WATER-DISPERSIBLE AMIDO-QUATERNARY AMMONIUM SALTS

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This invention relates to new and novel compositions of matter, and particularly to amido quaternary ammonium salts.

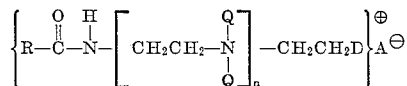
It is the principal object of this invention to produce a new class of water-dispersible amido quaternary ammonium salts useful as surfactants and foaming agents.

It is a special object of this invention to produce an improved new class of substances useful as ampholytic reagents and non-irritant shampoos.

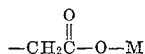
A further object of the invention is to provide novel compositions of matter which are useful in promoting water-wettability.

Other objects which appear hereinafter will be apparent from the more detailed description which follows.

In accordance with the invention, the novel water-dispersible amido quaternary ammonium salts constitute a special class of compounds having the general structural formula:



where R is an acyclic monovalent organic radical of from 5 to 21 carbon atoms in length, Q is a monovalent substituent selected from the group consisting of H and



D is a monovalent constituent from the group consisting of OM and



n is an integer of from 0 to 3 with the proviso that when n is 0, D represents



and with the further proviso that at least one occurrence of



is free from hydrogen atoms attached to the basic nitrogen atom when D is OM, M is from the group consisting of hydrogen and alkali metal and A is a halide anion.

The novel amido quaternary ammonium salts of this invention are produced by condensing a fatty monoamide of an organic fatty carboxylic acid containing from 5 to 21 carbon atoms in its acyl radical, with sodium chloroacetate or chloroacetic acid in the presence of base.

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To produce the monoamides of the invention, it is necessary to condense a fatty acid with a polyamine or substituted polyamine. The fatty acids which may be employed can be saturated or unsaturated, substituted or free from substitution. If a pure source of fatty acid is employed, it may vary in carbon length from 6 to 22 carbons. Examples of pure saturated acids are caproic, caprylic, capric, lauric, myristic, palmitic, stearic, arachidic, and behenic. Unsaturated pure fatty acids include those such as oleic, lauroleic, and palmitoleic. An example of a substituted fatty acid useful in the invention is ricinoleic. Mixtures of the above type fatty acids commonly found in vegetable oils, animal fats and oils, and marine fats and oils may also be used successfully. Examples of vegetable sources of fatty acids containing mixtures in various proportions are coconut oil, linseed oil, olive oil, palm oil, peanut oil, tongue oil, and rapeseed oil. Animal and marine sources of fatty acids containing saturated and unsaturated fatty acid substituents are lard, tallow, and sardine oil. Any fatty acid or mixtures of fatty acids whether pure or from impure sources may be employed without departing from the spirit of the invention as long as they contain from 6 to 22 carbon atoms in their chain length.

Preferred fatty acids are those contained in coconut vegetable oil. A typical coconut vegetable oil may contain fatty acids varying in length from 8 to 18 carbon atoms. These fatty acids from coconut oil may be saturated or unsaturated.

Esters of the fatty acids may also be employed without departing from the scope of the invention. The methyl or ethyl esters of the fatty acids may be easily condensed with the polyamines or substituted polyamines with ready removal of methanol or ethanol occurring.

The polyamines that may be condensed with the above fatty acids or fatty esters to produce the monoamide may be either polyamines or hydroxy-substituted polyamines. Examples of these types of amines are aminoethyl ethanolamine, diethylene triamine, ethylene diamine, triethylene tetramine, and tetraethylene pentamine. Any polyamine or substituted polyamine of the type described above may be used, with the only proviso being that the compound contain a free amino group available for quaternization subsequent to its mono-amidification with the described fatty acids.

Particularly useful polyamines are diethylene triamine and aminoethyl ethanolamine.

The amidification reaction is easily carried out by heating 1 mol of the polyamine or substituted polyamine with 1 mol of the fatty acid at temperatures from 100 to 200° C. for 1 to 8 hours, during which time 1 mol of water is removed. Preferred temperature ranges are from 120 to 180° C. for a period of from 2 to 6 hours. To facilitate easy removal of water, an organic azeotrope may be employed, such as benzene, toluene, or xylene.

To synthesize the quaternary derivatives of the monoamides, it is necessary to condense the fatty acid monoamide with an excess of sodium chloroacetate or chloroacetic acid in the presence of an alkali metal hydroxide.

The amount of alkylating agent used must be sufficient to quaternize at least 1 basic nitrogen atom of the monoamide. If, for example, the only free nitrogen atom available to enter into the quaternization reaction is a secondary nitrogen atom, it is sufficient to add 2 mols of sodium chloroacetate or chloroacetic acid in the presence

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of base. However, if the nitrogen atom available for the quaternization reaction is a primary nitrogen atom, it is necessary to add at least 3 mols of alkylating reagent. It is understood that polyquaternaries may be easily prepared by merely adding the requisite amount of quaternization reagent, depending upon the degree of quaternization required in the molecule. Various degrees of alkylation may also exist in the compositions of the invention, depending upon the various polyamine or substituted polyamine employed in amidification reaction. It is only necessary that at least one nitrogen atom be fully reacted to produce a quaternary ammonium salt.

Generally, the monoamide is added to a solution of sodium chloroacetate in base at room temperature. The solvent used for the quaternizing agent may be either water or a polar organic solvent such as isopropyl alcohol or ethanol. Mixtures of water and lower alkyl polar organic solvents may also be used. The mixture is then heated from 1 to 6 hours at a temperature of from 60 to 130° C. Under the preferred reaction condition, the quaternization reaction step is run from 1 to 4 hours at temperatures from 70 to 110° C. If necessary, additional base may be added to neutralize the amine hydrohalide salt formed during the earlier steps of alkylating prior to quaternizing. For every mol of sodium chloroacetate condensed upon the monoamide replacing the hydrogen atom of the basic nitrogen atom, it is necessary that there be at least one mol of base present to neutralize the amine salt formed. The addition of the final mol of sodium chloroacetate in which the nitrogen atom is quaternized requires no neutralization since no replaceable hydrogens are released. However, it has been found that the more preferred method of preparing the quaternary salts involves the use of excess alkali metal hydroxide. Any alkali metal hydroxide compound may be used to neutralize the hydrohalide amine salt, but the preferred bases are sodium hydroxide and potassium hydroxide.

The preparation of the compounds of the present invention is illustrated by the examples given herein below:

EXAMPLE I

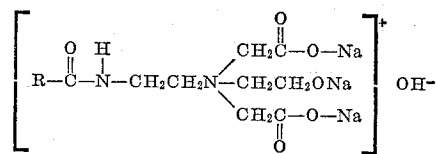
This example illustrates a typical method of producing the monoamides of the invention. 436 (2 mols) of the methyl ester of coconut oil fatty acid (molecular weight of 218) and 208 parts (2 mols) of aminoethyl ethanolamine were added to a 3-neck, round-bottom 1-liter flask equipped with a stirrer, thermometer, and a Dean and Stark trap connected between the flask and a reflux condenser. The reagents were mixed vigorously at room temperature and then heated rapidly to 155° C. The temperature was maintained between 155 and 175° C. by means of a heating mantle and variable transformer. The total reaction time at the above temperature range was 5 hours, during which time 62.5 parts of methanol were collected. The theoretical amount of methanol as a by-product of the reaction was 64 parts.

EXAMPLE II

This example illustrates the ease and facility of quaternizing the monoamide produced in Example I. To a 3-neck, round-bottom, 1-liter flask equipped with a stirrer, thermometer, and reflux condenser was added 60 parts of sodium chloroacetate (½ mol) and 26 parts of sodium hydroxide, 170 parts of water, and 50 parts of ethanol. To the quaternizing mixture was added 73 parts (¼ mol) of the coconut oil monoamide produced in Example I. The monoamide was added slowly and with vigorous agitation at a temperature of 20° C. During the addition, the temperature was maintained at 20° C. by the use of a cooling bath. The monoamide was added over a period of ½ hour. After the addition was completed, the mixture was heated to 95° C. slowly, and maintained at that

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temperature for a period of 2 hours. During this time, the pH of the mixture dropped from 14 to 8.5 due to the depletion of the sodium hydroxide through the neutralization action. After heating for 2 hours, 4 additional parts of sodium hydroxide were added in 10 ml. of water to bring the pH to 14 and the mixture was stirred and heated at 95° C. for another additional hour. The pH remained at 14 after this additional heating which indicated the reaction was essentially complete. The solution obtained was a slightly viscous, straw-colored liquid. The final product obtained, which is soluble in the water-ethanol solvent, may be represented by the formula:



where R is an acyclic fatty acid radical of the type found in coconut vegetable oil.

EXAMPLE III

576 parts of oleic acid (2 mols) and 208 parts of aminoethyl ethanolamine (2 mols) were mixed and heated under the same reaction conditions outlined in Example I. The monoamide was analyzed and found to have a neutral equivalent of 370. The theoretical neutral equivalent of the oleyl monoamide is 372-374.

EXAMPLE IV

To 60 parts (½ mol) of sodium chloroacetate contained in 26 parts of sodium hydroxide and 110 parts of water was added 93 parts (¼ mol) of the oleic acid monoamide prepared in Example III. The monoamide was added slowly, as illustrated in Example II and the temperature was maintained at 20° C. by the use of a cooling bath. The quaternization was then completed at the requisite temperature and heating time in a manner similar to that outlined in Example II. The final product may be represented by the formula of Example II where R is an acyclic fatty acid radical of the type found in oleic acid.

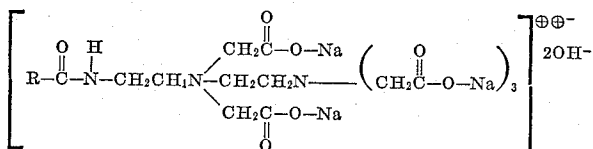
EXAMPLE V

To a 3-neck, round-bottom, 1-liter flask equipped with a stirrer, thermometer, and reflux condenser was added 250 parts of coconut vegetable oil fatty acid (1 mol). The fatty acid was heated to 90° C. and to this was added 309 parts of diethylene triamine (3 mols). The reaction mixture was heated to 160° C. and held at this temperature by means of a heating mantle and variable transformer for 3 hours. At the completion of the reaction, the theoretical amount of water (18 parts) as a by-product of the amidification condensation had distilled off. The reaction mixture was cooled down to 90° C. and the excess diethylene triamine was vacuum-distilled off between 90 and 100° C. at a pressure of 2 millimeters. The neutral equivalent of the monoamide was 150, which indicates an essentially pure monoamide product. A solution of 118 parts of chloroacetic acid, 50 parts of sodium hydroxide, and 110 ml. of water was then prepared. To this mixture was slowly added, at 20° C. with cooling, 75 parts (¼ mol) of the monoamide produced from the above reaction. The time of addition was ½ hour. After all the monoamide had been added to the quaternizing mixture, the temperature of the reaction was raised to 85° C. The temperature was held between 85 and 90° C. for 2 hours, after which time, 10 additional parts of sodium hydroxide in 20 parts of water was added. The heating was then continued for an additional hour at 95° C. The final product obtained was a diquaternary

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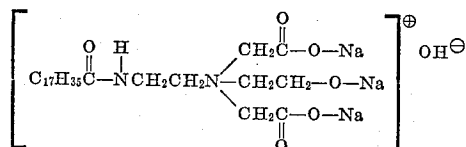
where R is a coco fatty acyclic radical ranging in carbon content from C₈-C₁₈.

4. A water-dispersible amido quaternary ammonium salt having the formula:



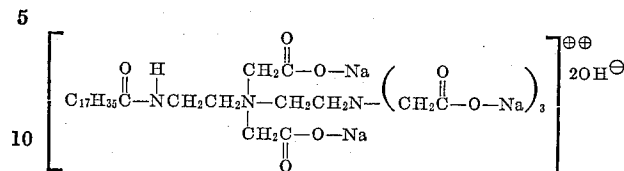
where R is a coco fatty acyclic radical ranging in carbon content from C₈-C₁₈.

5. A water-dispersible amido quaternary ammonium salt having the formula:



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6. A water-dispersible amido quaternary ammonium salt having the formula:



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