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3,154,489

SURFACE ACTIVE COMPOSITIONS

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This invention relates generally to surface active agents, and more particularly to quaternary ammonium salts.

The present application is a continuation-in-part of our copending application Serial No. 787,335, filed January 19, 1959, now abandoned.

The quaternary ammonium salts, being "cationic" or "cation-active" agents, are not compatible with anion-active materials. Generally, the quaternary ammonium salts are precipitated or rendered inactive by organic anion-active materials, such as soaps, alkyl aryl sulfonates, other anionic synthetic detergents, and carboxymethyl cellulose. Also, the polyvalent inorganic anions, such as the phosphates and sulfates, act as precipitants of the quaternary ammonium salts.

This incompatibility is a serious problem as the effective utilization of the quaternary ammonium salts for their functional benefits is restricted thereby. For example, the quaternary ammonium salts are very effective as softening agents for hair and cellulosic materials, such as textiles and tissue paper. However, when the quaternaries are used as the active ingredients for imparting "softness" to the treated material, traces of any of the aforementioned precipitants, which are usually carried over with the base material from previous treatments, either precipitate or render the quaternary inactive. Consequently, the possible benefits which could be obtained from the ammonium salts are lost.

A second problem arises out of the fact that if a second material is added to the quaternary ammonium salt, it is found that the second material does not aid the quaternary ammonium salts in their function as softening agents, but constitute in effect waste material as far as such softening function is concerned, and in addition it is found that such added material does not tend to overcome the waterproofing characteristic of the quaternary ammonium salt, etc.

We have found that a surface-active composition comprising a quaternary ammonium salt and a polyoxyethylene fatty amine condensation product is highly compatible with anion-active materials, while at the same time the condensation product add a quota of softening activity to that of the quaternary ammonium salt. Also, it has the additional effect of conditioning the textile, etc. material for rewetting. Instead of being an inert or waste material as far as actively inducing softening is concerned, the ethoxylated fatty amine condensation product contributes actively to the softening function of the complete composition.

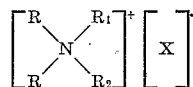
Therefore, a principal object of the present invention is to provide surface-active compositions, containing quaternary ammonium salts, which are compatible with anion-active materials. A further object is to provide such compositions in which effective softening effects are produced through the added softening activity provided by the ethoxylated amine component. A still further object is to provide such a composition which may be employed in the treating of textiles and other fibers for imparting softness thereto, while at the same time conditioning the material for rewetting. Other specific objects and advantages will appear as the details of the invention are set out.

The surface active compositions of the instant invention comprise a quaternary ammonium salt and an ethoxylated amine, a polyoxyethylene-fatty amine condensation

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product containing 15 to 60 moles ethylene oxide. Coloring and perfume may, if desired, be added to the aqueous dispersions. The compositions may be in the form of free flowing powders or aqueous dispersions.

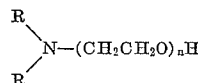
The quaternary ammonium salt component of the surface active compositions of the invention has the formula



wherein R represents benzyl or an alkyl group containing 1 to 3 carbon atoms, R_1 represents benzyl, or an alkyl group containing 1 to 3 carbon atoms, or an alkyl group containing 12 to 18 carbon atoms, R_2 represents an alkyl group containing 12 to 18 carbon atoms, and X represents an anion, such as halogen, acetate, phosphate, nitrite, and methyl sulfate radicals. The carbon chain of the alkyl group having 12 to 18 carbon atoms may be straight or branched, and saturated or unsaturated. In the preferred embodiments of the invention, this group is derived from long chain fatty acids. The preferred ammonium salt is a dialkyl dimethyl ammonium chloride or an alkyl trimethyl ammonium chloride wherein the alkyl group is derived from hydrogenated tallow.

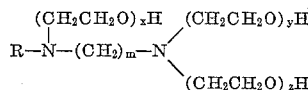
The polyoxyethylene-fatty amine condensation products that have peculiar efficacy as the other active component of the compositions of the instant invention may be either mono- or di-tertiary fatty amines containing 15 to 60 moles of ethylene oxide.

The mono-tertiary fatty amines have the general formula



wherein R is an alkyl group having 8 to 18 carbon atoms in its carbon chain, and n is an integer from 15 to 60.

The di-tertiary amines, commonly known as diamines, have the general formula



wherein R is an alkyl group having 8 to 18 carbon atoms in its carbon chain, m is an integer from 2 to 3, and the sum of x+y+z is an integer from 15 to 60.

In the preferred embodiments of the invention, the R group of the ethoxylated amine is derived from long chain fatty acids. Also, the fatty acids can be derived from mixtures, such as are prepared from tallow, coconut oil, and soybean oil. The ethoxylated coco amine products are preferred for use in the surface active compositions of this invention.

The effective proportions of the active ingredients of the compositions were found to be that for every part by weight of the quaternary ammonium salt there should be 0.1 to 2.0 parts by weight of the fatty amine-polyoxyethylene condensation product. In other words, the weight ratio of quaternary ammonium salt to polyoxyethylene-fatty amine condensation product is within the range of from 10:1 to 1:2. When the components are present in these ratios, the resulting compositions are stable and may be diluted with water for ease of handling and addition to other aqueous media containing the base materials to be treated therewith. When the compositions are so used, the presence of any of the aforementioned anionic precipitants does not render the quaternary ammonium salt ineffectual. As a consequence thereof, it is now possible to utilize quaternary ammonium salts under conditions that were considered heretofore adverse.

We have found that an excellent treating composition for softening fibers and conditioning them for rewetting is prepared by combining a quaternary ammonium salt containing substantially no moles of ethylene oxide but containing an alkyl group having 12 to 18 carbon atoms with a condensation product of a fatty amine containing an alkyl group having 8 to 18 carbon atoms with 15 to 60 moles of ethylene oxide, the weight ratio of the salt to the condensation product being from 10:1 to 1:2.

Having described in detail each of the component compounds constituting the surface active compositions of the present invention, it therefore becomes convenient to present a number of specific and illustrative completed compositions, the parts being given by weight.

Example I

Dimethyl distearyl ammonium chloride	83.3
Dilauryl polyoxyethylene tertiary amine containing 15 moles of ethylene oxide	16.7

Example II

Diethyl dilauryl ammonium acetate	50.0
Dimyristyl polyoxyethylene tertiary amine containing 40 moles of ethylene oxide	50.0

Example III

Dibenzyl dipalmityl ammonium chloride	33.3
Distearyl polyoxyethylene tertiary amine containing 60 moles ethylene oxide	66.7

Example IV

Dipropyl distearyl ammonium phosphate	90.9
N-capryl-N,N'-polyoxyethylene ethylene diamine containing 45 moles ethylene oxide	9.1

Example V

Trimethyl stearyl ammonium chloride	35.0
Dicapryl polyoxyethylene tertiary amine containing 15 moles ethylene oxide	65.0

Example VI

Dimethyl distearyl ammonium methyl sulfate	50.0
Dilauryl polyoxyethylene tertiary amine containing 30 moles ethylene oxide	50.00

Example VII

Trimethyl lauryl ammonium methyl sulfate	70.0
N-lauryl-N,N'-polyoxyethylene propylene diamine containing 45 moles ethylene oxide	30.0

Example VIII

Trimethyl palmityl ammonium acetate	40.0
N-stearyl-N,N'-polyoxyethylene propylene diamine containing 60 moles ethylene oxide	60.0

Example IX

Dimethyl benzyl stearyl ammonium nitrite	50.0
Dimyristyl polyoxyethylene tertiary amine containing 15 moles ethylene oxide	50.0

Example X

Dimethyl benzyl myristyl ammonium chloride	83.3
Disoya polyoxyethylene tertiary amine containing 30 moles ethylene oxide	16.7

Example XI

Trimethyl stearyl ammonium chloride	90.9
Dicoco polyoxyethylene tertiary amine containing 35 moles ethylene oxide	9.1

Example XII

Dimethyl distearyl ammonium methyl sulfate	75.0
N-soya-N,N'-polyoxyethylene propylene diamine containing 25 moles ethylene oxide	25.0

Example XIII

Trimethyl palmityl ammonium chloride	60.0
N-tallow-N,N'-polyoxyethylene propylene diamine containing 40 moles ethylene oxide	40.00

Example XIV

Dimethyl distearyl ammonium methyl sulfate	50.0
N-coco-N,N'-polyoxyethylene ethylene diamine containing 50 moles ethylene oxide	50.0

Example XV

Comparative tests were carried out to determine the effect of our surfactant composition as to softening and rewet results, using as comparisons the same quaternary compounds with non-ionic substitution materials. These tests comprise the present example and the following Examples XVI and XVII.

Three parts of Arquad 2HT (dimethyl dihydrogenated tallow quaternary ammonium compound) were combined with one part of Ethomeen 2C/25 (dicoco amine containing 15 moles of ethylene oxide). The above compositions were based on the weight of the material treated and were added to the final rinse in the treatment for textiles.

A similar test was made employing Arquad 2HT alone. It was found that the composition containing Arquad 2HT and Ethomeen not only provided increased softening but substantially retained the wettability property of the textiles.

Example XVI

The test was carried on as described in Example XV above except that the following compositions were compared:

#B Arquad 2HT (3 parts)—Ethomeen 2C/25 (1 part)
#4 Arquad 2HT (5 parts)—Atlas G-1256 (1 part)—polyoxyethylene sorbital esters of fatty acid)—nonionic

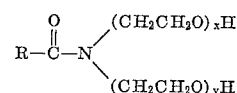
The test results showed #B to have increased softening and rewet effect.

Example XVII

Tests were carried on as described in Example XV except that the following compositions were tested:

#1 Arquad 2HT (3 parts)—Ethomeen 2C/50 (1 part)
#2 Arquad 2HT (3 parts)—Ethomid HT/15 (1 part)

Ethomid HT/15 has the following formula:



in which R is hydrogenated tallow and x plus y equals 5.

Ethomid is complete non-ionic. Its substitution reduced softening. #2 composition had poor softening and no rewet, while #1 composition had excellent softening and good rewet.

Example XVIII

Insofar as compatibility is concerned, whiteness retention was measured when a detergent (Tide) was added to a final rinse containing Arquad 2HT. The numbers set out below refer to a drop in reflectance from a blank for the cloth. The additives and results are listed as follows.

Non-ionic	
Ethomeen 2C/38	4.0
Polyglycol 1,000	7.0
Polyglycol 20,000	10.0
Polyvinyl alcohol	6.8

Example XIX

The stability of 3.5% Arquad 2HT formulation in waters of high electrolyte content (Los Angeles water) was determined. Separation occurred with the use of Arquad 2HT alone. However, there was good stability when Arquad 2HT (3 parts) was combined with Ethomeen 2C/25 (1 part).

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The surface active compositions of the instant invention are particularly useful in the manufacture of textiles and tissue paper for improving surface softness. Each of the above compositions was tested at concentrations of from 0.1% to 0.3% based on the weight of the material treated. For textiles, the surface active composition was added to the final rinse. In the manufacture of tissue paper, the compositions were dissolved in hot water and then added to the pulp in the beater with other paper ingredients. The mixture was digested for about one-half hour prior to felting. In all cases, the presence of trace precipitants, hereinbefore set forth, in the aqueous media did not affect adversely the quaternary ammonium salt. Surface softness was obtained with all compositions. When the same quaternary salts were used alone, the material was insufficiently treated and the desired degree of surface softness was not obtained.

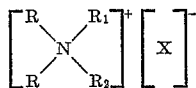
Additional tests were made to determine the efficacy of the surface active compositions of the instant invention for effecting softening of hair and clothes after washing with conventional soaps and/or detergents with or without water softening agents being present during the washing and intermediate rinsing steps. The fabric or hair softener is usually added to the final rinse. However, the intermediate rinses usually do not remove all of the washing or cleaning agents or water softeners prior to the final rinse. Consequently, traces of anionic materials are usually present during the final rinse. Heretofore, the use of quaternary ammonium salts under these conditions has not been satisfactory. The cationic quaternary ammonium salts reacted with the anionic materials to form insoluble products. The tests of each of the above compositions in laundry equipment showed that the presence of trace amounts of the cleaning agents with or without water softening materials, such as the polyphosphates, was not detrimental to the effectiveness of the quaternary ammonium salt. Here again, the desired degree of softness was only obtainable when the polyoxyethylene-fatty amine was present.

Aqueous dispersions were prepared from the compositions hereinbefore set forth so that the active components were present at a 0.15% concentration. These dispersions were used as hair rinses and found to be satisfactory without precipitation of the quaternary salt which did occur when the ammonium salt was used as the sole softening agent.

While in the foregoing specification various embodiments of this invention have been set forth and many details thereof elaborated for the purpose of illustration, it will be apparent to those skilled in the art that this invention is susceptible to other embodiments and that many of these details can be varied widely without departing from the basic concept and spirit of this invention.

We claim:

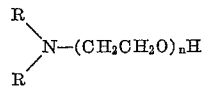
1. A treating composition for softening fibers and conditioning them for rewetting, comprising a quaternary ammonium salt having the formula



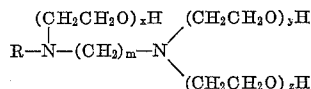
where R is selected from the group consisting of an alkyl

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group containing 1 to 3 carbon atoms and benzyl, R₁ is selected from the group consisting of an alkyl group containing 1 to 3 carbon atoms, an alkyl group containing 12 to 18 carbon atoms and benzyl, R₂ is an alkyl group containing 12 to 18 carbon atoms, and X is an anion; and an ethoxylated amine selected from the group consisting of a tertiary amine having the formula



where R is an alkyl group containing 8 to 18 carbon atoms, and n is an integer from 15 to 60, and a diamine having the formula



where R is an alkyl group containing 8 to 18 carbon atoms, m is an integer from 2 to 3, and the sum of x+y+z is an integer from 15 to 60, the weight ratio of the quaternary ammonium salt to ethoxylated amine being from 10:1 to 1:2.

2. A treating composition for softening fibers and conditioning them for rewetting, said composition consisting essentially of dimethyl distearyl ammonium chloride and dilauryl polyoxyethylene tertiary amine containing 15 to 60 moles ethylene oxide, the weight ratio of said chloride to said amine being from 10:1 to 1:2.

3. A treating composition for softening fibers and conditioning them for rewetting, said composition consisting essentially of dimethyl distearyl ammonium methyl sulfate and dilauryl polyoxyethylene tertiary amine containing 15 to 60 moles ethylene oxide, the weight ratio of said sulfate to said amine being from 10:1 to 1:2.

4. A treating composition for softening fibers and conditioning them for rewetting, said composition consisting essentially of trimethyl stearyl ammonium chloride and dicoco polyoxyethylene tertiary amine containing 15 to 60 moles ethylene oxide, the weight ratio of said chloride to said amine being from 10:1 to 1:2.

5. A treating composition for softening fibers and conditioning them for rewetting, said composition consisting essentially of dimethyl distearyl ammonium methyl sulfate and N-soya-N,N'-polyoxyethylene ethylene diamine containing 15 to 60 moles ethylene oxide, the weight ratio of said sulfate to said diamine being from 10:1 to 1:2.

6. A treating composition for softening fibers and conditioning them for rewetting, said composition consisting essentially of trimethyl palmityl ammonium chloride and N-tallow-N,N'-polyoxyethylene propylene diamine containing 15 to 60 moles ethylene oxide, the weight ratio of said chloride to said diamine being from 10:1 to 1:2.

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