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DIFATTY ALKYL-DILOWERALKYL QUATERNARY AMMONIUM COMPOUNDS

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ABSTRACT OF THE DISCLOSURE

Quaternary ammonium compounds in which two substituents on the nitrogen are derived from the residual fatty acid monomer left after polymerization of higher fatty acids and the remaining two substituents are lower alkyl groups. These compounds are intended as clothes softener compounds and have improved rewetting characteristics.

The present invention relates to certain novel fatty quaternary ammonium compounds and to their use for the softening of textiles.

A number of fatty quaternary ammonium compounds have been used in the past for textile softening purposes. One very commonly in use at the present time is dimethyl difatty quaternary ammonium chloride, in which the fatty group is predominantly a C_{18} saturated group. These compounds are generally made from a starting material rich in a C_{13} saturated fatty acid, particularly stearic acid, such as tallow. While these prior fatty quaternary ammonium compounds have been satisfactory insofar as their softening properties are concerned, they have been subject to the disadvantage that they have a water-proofing effect upon textiles through repeated use. Thus, for example, bath towels repeatedly subjected to the use of the softening compounds have a reduced absorbency and, therefore, are less desirable than towels having the original absorbency.

It has now been discovered that it is possible to prepare fatty quaternary ammonium compounds which have approximately the same softening properties as the dimethyl dihydrogenated tallow quaternaries commonly employed at the present time, by preparing such quaternaries using as a starting material the monomer fatty acid which is a residue left after the polymerization of unsaturated fatty acids. These quaternary compounds have approximately the same softening properties as the above mentioned compounds but the rewetting characteristics are far superior.

The novel compounds from the present invention have the following formula:

$$\begin{matrix} & R_3 & \\ & | & \\ R_1 & -N^+ & -R_2 \quad X^- \\ & | & \\ & R_3 & \end{matrix}$$

in which R_1 and R_2 are lower alkyl groups containing from 1 to 4 carbon atoms and R_3 is the hydrocarbon radical corresponding to the residual fatty acid monomer left after the polymerization of higher unsaturated fatty acids containing from 8 to 24 carbon atoms, and X is a quaternary ammonium anion. R_1 and R_2 may be methyl ethyl, propyl or butyl, either straight or branched chain and preferably are both methyl. X may be any conventional quaternary anion such as a chloride, sulfate, etho sulfate, nitrate and the like. Because of the ease of preparation of compounds by methylation with methyl chloride the chloride anion is preferred.

As was pointed out above, R_3 is the hydrocarbon group derived from the residual monomer from the polymerization of unsaturated higher fatty acids containing from 8 to 24 carbon atoms. Fatty acid polymers of a type re-

ferred to immediately above are articles of commerce. They have been prepared by the simple thermal polymerization of unsaturated fatty acids and also by the catalytic polymerization of such fatty acids, for example by means of clay catalysts. In these polymerizations a mixture of fatty acids containing from 8 to 24 carbon atoms usually derived from natural fat oil are employed as starting material. When these acids are subjected either to a thermal polymerization for example at temperatures of 260 to 300° C. or by catalytic thermal polymerization for example in the presence of clay at temperatures from say 180 to 250° C., the fatty acids polymerize. In the thermal process the polyunsaturated fatty acids polymerize most easily and the residual monomer is composed almost entirely of mono-unsaturated fatty acids together with any saturates which may have been present in the starting material. In the catalytic process both the polyunsaturated and the mono-unsaturated acids polymerize and there is accordingly a lesser residue of monomer, but again the unsaturated acids in the monomer are almost entirely mono-unsaturated. During the polymerization process the monomer, while it does not polymerize, is modified in structure so that it no longer has either the physical or chemical characteristics of the original starting material. In fact, it has been so modified that it usually no longer finds use for the same purposes for which the fatty acid in its unmodified form may be used. Consequently this residual monomer has in the past found restricted use in commerce and in many instances was burned as fuel since it had greater value for this purpose than for many of conventional chemical uses to which it is adapted. Some concepts of possible structure for the residual monomer are to be found in the Journal of the Oil Chemists Society, 26, No. 6, p. 278 (1948), and Industrial and Engineering Chemistry, 44, 1113 (1952).

While it has been difficult to find suitable uses for this monomer in conventional applications, surprisingly enough when it is converted into a fatty quaternary ammonium compound it possesses certain unique properties which render it superior to materials produced from higher priced raw materials. One such unique property involves the discovery that the quaternary compounds have softening properties comparable to other commercially used compounds but have far superior rewetting characteristics as will be demonstrated in further detail hereinafter.

In preparing quaternary ammonium compounds from the residual monomer the monomer is converted to the nitrile by reaction with ammonia in the conventional manner. The nitrile thus obtained is then hydrogenated in the presence of a catalyst to produce a secondary fatty amine $(R_3)_2NH$. The production of the secondary amine is carried out in a manner well understood in the art. The secondary amine is then converted to the quaternary compound by the reaction with typical alkylating agents such as methylchloride. Again the alkylation reaction is well known in the prior art and forms no part of the present invention.

The residual monomer starting material contains an appreciable amount of fatty acids still possessing some residual unsaturation. In general, quaternary ammonium compounds prepared from this residual monomer have excellent softening properties and excellent rewetting properties. However, if the fatty group in the quaternary compound possesses substantial unsaturation, there is a tendency for the textile materials softened with these compounds to take on a yellow cast which is generally considered undesirable. This tendency toward yellowing does not interfere with the softening properties but merely raises some aesthetic objections; accordingly, it is pre-

ferred to reduce the amount of unsaturation in the fatty group so the resultant quaternary compound has an iodine number of 40 or less. This may be accomplished by suitably hydrogenating the monomer starting material or it may be accomplished by the hydrogenation conditions encountered in forming the amine from the nitrile. While it is possible to reduce the iodine value by hydrogenation, it is extremely difficult to get an iodine number approaching zero. Apparently, to some extent, the nature of the unsaturation has been modified during the polymerization process so that not all double bonds may be saturated with hydrogen. It is possible, however, to hydrogenate the iodine value below 40 and indeed it may be possible to reduce the iodine value to 5 or less. These hydrogenated products are superior with reference to any yellowing tendencies.

In the preparation of a textile softening material from the quaternary compound, the quaternary is usually dispersed in an aqueous medium either by itself or with the assistance of an organic solvent, such as a lower aliphatic alcohol, for example, isopropanol. As a convenient manner of distributing the softener on the textile surface, the softening agent may be used in a concentration of the order of magnitude of 0.00707% by weight of the solution. Conventionally these are used at levels of approximately 0.00125 gram of softening compounds per gram of dry textiles. The amount of softener used can vary considerably but generally is within the range of 0.0005 to 0.005 gram per gram of dry textile.

The softening of the various compounds was determined in the following test: Swatches of white birdseye cotton (36" x 12") are placed in a normal 8-pound wash load and are washed at 140° F. with a conventional household detergent in the same manner as is done in a regular household wash. The swatches are washed in an automatic washer with a 6-minute wash cycle followed by a 1-minute spray rinse and a 4-minute final deep rinse. The swatches are then dipped in solutions of the compound being tested.

The dipping is done in a water bath using beakers and agitation is provided by means of a stirring rod. The dipping is carried out duplicating the conditions in the last rinse of the automatic wash machine which are: 4 minutes of agitation at 100° F. using a 0.00707% solids solution concentration (for normal use level) and a 17.7 to 1 solution to dry fabric ratio. This results in a normal use level of 0.00125 gram per gram of dry fabric. The swatches are allowed to stand 1 minute following agitation and the dipping solution is then poured off and the swatches are spun in the washer to remove excess dipping solution. The swatches are then allowed to air dry before being cut up for testing. After drying, each swatch is cut into twelve samples (4" x 4"). The samples are marked and placed in a room under controlled temperature and relatively humidity until tested (50° relative humidity at 72° F.).

The panel testing is carried out by a panel of twelve women who test in duplicate—making a total of twenty-four tests. Each test consists of comparing the softness of three pairs of samples. These pairs have been treated as follows:

(1) One and one-half normal use level test compound vs. normal use level of the standard compound,

(2) Normal use level test compound vs. normal use level of the standard compound, and

(3) Normal use level test compound vs. one-half normal use level of the standard compound. The panel is asked to indicate which sample of each pair they think is the softer. The results are treated statistically using the method of X^2 (chi-squared) where

$$X^2=\Sigma\left(\frac{o-e}{e}\right)^2$$

o=observed, e=expected. (Reference: Applied General Statistics, by Croxton and Cowden, copyright 1939, by Prentice-Hall, Inc.) The value of X^2 is then looked up in a significance table to see if the results are significant and if so, at what level of significance. From these results it is possible to determine if the compound is as good as the standard compound, one-half as good as the standard compound or somewhere in between one-half as good and as good as the standard compound in softening efficiency.

By the above test, it was determined that the compounds of the present invention were approximately equal in softening ability to the standard compound used for comparison.

The rewetting characteristics were determined as follows: Swatches of birdseye cotton (24" x 12") are washed in an automatic washer, using the conventional household detergent but are removed before the final deep rinse. Two swatches are dipped in a normal concentration solution of the standard compound and two swatches are dipped in twice the normal concentration of the compound being tested. The dipping procedure is the same as used in the above-described softener test. One of the swatches dipped in the normal concentration of the standard compound and one of the swatches dipped in twice the normal concentration of the test compound are then put through an identical wash-soft cycle so that the rewetting test is run on samples dipped in normal and twice the normal softener use levels, both after one and after two wash-soften cycles. After dipping, the swatches are air dried and each swatch cut into two 10" x 10" samples. The samples are marked and placed in a room under controlled temperature and relative humidity (50% relative humidity at 72° F.) for conditioning. Testing was carried out under these temperature and humidity conditions.

The rewetting test consists of dropping drops of water on a sample of treated cloth from a buret and determining the average length of time it takes for the drops to soak into the cloth. The buret is held about ⅜ inch from the sample and is adjusted so that it delivers approximately one drop of water every five seconds. The sample is held over a six-inch metal framework so that all parts of the cloth are under equal tension. The sample was held taut over the framework by means of a 137 gram weight clipped to each side of the sample by six-inch jaws. A drop of water is dropped on the cloth and the time taken for the disappearance of this drop is taken as the rewetting time. Ten such tests are run on each sample, making a total of twenty tests for the two samples. The average rewetting time is then the average of these twenty tests.

EXAMPLE

Tall oil fatty acids were heated at atmospheric pressure in the presence of 10% montmorillonite clay at a temperature of 200–230° C. for 4 hours. The reaction mixture was then filtered to remove the clay and the filtrate was subjected to vacuum distillation to remove the residual monomer.

This monomer was then converted to the nitrile by heating it in a pot reactor at a temperature of 250–300° C. for a period of 5–10 hours while blowing ammonia through the reaction mixture. The reaction is essentially complete when the acid value is reduced to less than one and the amide content is below 2%. At this point, the reaction mixture is subjected to vacuum distillation to remove the nitrile.

The nitrile is converted to the secondary amine by hydrogenating it with Raney nickel at 200 pounds per square inch pressure at a temperature of around 225° C. while periodically removing ammonia formed during the reaction. Upon completion of the reaction, the reaction mixture was cooled to about 100° C. and then filtered to yield a product having a total amine content of 99.0%, a secondary and tertiary amine content of 93.3 and a tertiary amine content of 3.7%.

During the course of the hydrogenation, the iodine value was reduced to 12.3.

This secondary amine was then quaternized with methylchloride in the presence of isopropanol and alkali. The reaction was conducted at 70 to 80° C. for a period of about 15 hours after which the product was cooled and filtered to yield a product which was 69.1% solids and which contained 68.0% quaternary.

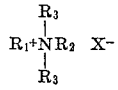
This quaternary was then dispersed in water to yield a solution containing 0.00707% solids and this solution was used to treat fabrics as described above. As indicated the product had essentially equal softening characteristics but decidedly improved rewetting characteristics. The compound showed rewetting times in the general area of 5 to 18 seconds as compared with rewetting times in the general area of 100 to 300 seconds for the standard used for comparison, which was a dimethyl dihydrogenated tallow ammonium chloride which is used in large volume in current clothes softeners.

Similar results were obtained with the quaternary ammonium chloride produced from residual monomer from the thermal polymerization of fatty acids.

While specific examples of the invention have been described, it will be evident that other variations of the invention are possible within the scope of the following claims.

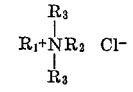
The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. Compounds having the following formula:



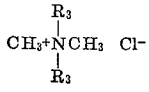
in which R_1 and R_2 are lower alkyl groups containing from 1 to 4 carbon atoms and R_3 is the hydrocarbon radical corresponding to the residual fatty acid monomer left after the polymerization of higher unsaturated fatty acids containing from 8 to 24 carbon atoms, and X is a quaternary ammonium anion.

2. Compounds having the following formula:



in which R_1 and R_2 are lower alkyl groups containing from 1 to 4 carbon atoms and R_3 is the hydrocarbon radical corresponding to the residual fatty acid monomer left after the polymerization of higher unsaturated fatty acids containing from 8 to 24 carbon atoms.

3. Compounds having the following formula:



in which R_3 is the hydrocarbon radical corresponding to the residual fatty acid monomer left after the polymerization of higher unsaturated fatty acids containing from 8 to 24 carbon atoms.

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