Quaternary ammonium derivatives of bisimidazoline compounds which are characterized in having a long chain aliphatic substituent in the 2 and 2' positions of the respective rings and wherein the 1, 1' linking entity is an alkylene radical or polyalkylene segments internally joined by an amino or amido nitrogen atom(s). These derivatives are highly effective fabric softeners having unique physical properties.
3,855,235

QUATERINARY AMMONIUM DERIVATIVES OF BISIMIDAZOLINE COMPOUNDS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to quaternary ammonium derivatives of a class of bismidazolines provided by the cyclization of condensation products of certain polyalkylene amines with fatty acids or functional equivalents thereof.

2. Description of the Prior Art

Compounds containing the imidazole ring structure and further substituted in the number 2 position with a long chain aliphatic group are well known in the art. These compounds are cationic substances exhibiting surface active properties to the extent of rendering them useful cationic emulsifiers, flotation agents, corrosion inhibitors and the like. The imidazolines are of particular interest because they can be more readily and economically prepared than the aliphatic amines of comparable molecular weight and functional effectiveness in the uses noted.

Hereinbefore the imidazoline compounds referred to above have been prepared first condensing a higher fatty acid with a polyamine containing a secondary amine group in a gamma position with respect to at least one primary amine group. Following the foregoing step which leads to the formation of an amido substituted alkyne amine, same is cyclized to yield the imidazolone structure. Where the cyclized product contains a terminal primary amine group in the aliphatic residue such as those derived, for example, from diethylene trimine, it is known that these compounds can be advantageously modified by further condensation with a fatty acid.

It has also been proposed by the prior art that the quaternary ammonium derivatives of the aforesaid imidazolines are effective fabric softeners. As a matter of fact, a substantial proportion of the current softeners of commerce is of this type. Fabric softeners for household applications are exclusively marketed in the form of dilute aqueous dispersions thereof. Because of the viscous nature of the quaternary ammonium derivatives of the imidazolines, as well as those of the aliphatic amines mentioned hereinabove, it has been proven to be difficult to prepare the dilute dispersions and even more difficult to obtain such dispersions having requisite stability characteristics. It has, accordingly, been a continuing object of investigators in this field to develop fabric softeners having improved dispersibility and stability characteristics with the ultimate objective in mind of developing an effective softener which will provide a dilute aqueous dispersion having colloidal or pseudo soluble characteristics.

SUMMARY OF THE INVENTION

In accordance with the present invention, quaternary ammonium derivatives of a class of bismidazoline compounds are provided wherein the indicated compounds correspond to the following structural formula:

wherein R₁ is a C₅–C₈ hydrocarbyl group; n is an integer of from 0–4; R is a C₂–C₆ alkylene group; and A is hydrogen or an acyl group of the formula R₂ · C · in which R₂ has the meaning as aforesaid.

The quaternized products of the foregoing bismidazolines are remarkably unusual in that the dilute aqueous dispersions thereof have the appearance of being solutions of crystal-like clarity. Dilute aqueous dispersions in contemplation of the aforesaid statement are those containing from 2 to about 12 weight percent of the quaternized product.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preparation of imidazoline compounds of the type concerned herein basically involves the reaction of a higher fatty acid or functional equivalent thereof with a polyamine. The imidazolines are of a specific type of polyamine. Such polyamines are those having the following structural formula:

\[ \text{NH}_2 \text{CH}_2 \text{CH}_2 \text{NR} \text{(NHCHR)}_n \text{N} \text{HCH}_2 \text{CH}_2 \text{NH}_2 \]

wherein R represents a C₂–C₆ alkylene group, preferably ethylene. The preferred polyamine is triethylene tetramine. The latter amine as well as those otherwise corresponding to the structural formula given are commercially available. They are reported to be prepared by the ammonolysis of either an alkylene dichloride or an olefin; specifically ethylene, for realizing the preferred polyamines.

With respect to the applicable fatty acid reactants, substantially more latitude is afforded in the selection thereof than the polyamine. Broadly, the C₄–C₂₄ fatty acids are suitable for deriving the bismidazoline compounds useful in the practice of this invention. Representative of such fatty acids include: caproic, heptanoic, caprylic, capoic, decenoic, undecenoic, lauric, dodecenoic, tridecenoic, myristic, tetradecenoic, pentadecenoic, hexadecenoic, palmitic, heptadecenoic, stearic, oleic, nonadecenoic, eicosanoic, behenic, tetracosanoic and the like. The preferred fatty acids are the mixtures thereof derived from tallow, soybean or coconut oil. Tall oil fatty acids are exemplary of a naturally occurring mixture of acids suitable for the instant purposes.

Particularly preferred for obtaining the contemplated bismidazoline compounds is the mixture of fatty acids constituting tallow. The fatty acid reactant of the reactant form of the fatty acid itself, an alkyl ester thereof or the naturally occurring glyceride esters. As will be noted below, the glyceride ester form of the fatty acid will readily split in the course of the initial condensation of the acid and the polyamine reactant and the glycerol by-product can be removed from the reaction mixture. Since the naturally occurring glyceride form of the indicated animal and vegetable derived fatty acids are more economical than the free acids or the mono esters, it is particularly preferred to use these fatty acids in this form. In connection with this discussion of the suitable fatty acids for use in the practice of this invention, it is to be noted that the R₂ substituent of the respective imidazoline rings represents the hydrocarbyl group attached to the carboxyl group of the fatty acid from whence derived. Accordingly, when a mixture of
fatty acids is used, such as for example, tallow, the $R_1$ substituent collectively represents the mixture of hydrocarbyl residues associated with carboxyl groups of said fatty acids.

In effecting the initial condensation of the fatty acid and the polyamine such are merely heated at about 100 to 200°C, preferably employing a nitrogen sparge when the fatty acid is in the form of the free acid or mono ester thereof. In the case of utilizing the triglyceride form of the fatty acid, it is preferred to carry out the condensation at a slight pressure or under a mild reflux condition. In preparing the unmodified bisimidazolines contemplated herein, the selected polyamine and fatty acids are reacted in a relationship of about 0.9 to 1.5 moles of the polyamine for two moles of the fatty acid. Of course, when the triglyceride form of the fatty acids is used, one will employ two-thirds of a mole thereof in order to provide the two moles of fatty acid for combining with the polyamine in the relationship selected. As indicated, where a triglyceride oil is used, splitting to effect the in situ formation of the polyamido amine is readily accomplished in the reaction system concerned.

In those instances where the linking entity of the contemplated bisimidazolines contain one or more secondary amine groups such can be further modified completely or partially by reaction with a fatty acid or again a functional equivalent thereof such as a triglyceride oil. This type of further modification can be achieved after the cyclization step described herein below or sufficient added fatty acids can be included in the initial reaction product in order to achieve the extent of modification desired. The latter procedure is preferred.

The next step in deriving the bisimidazolines involves cyclizing the polyamido amine. This reaction is accomplished by heating the polyamido amine at a temperature between about 125° and 250°C under vacuum. Sub-atmospheric pressure conditions in the order of from 1 to 300 mm Hg suffice for this purpose. In those instances where the free fatty acid or a lower alkyl ester thereof is employed as a reactant, the use of moderate vacuum in the order indicated is generally observed. Where, however, the polyamido amine is derived from a triglyceride ester, it is advantageous to operate at the low levels of the indicated pressure range in order to effect the removal of the glycerine. The extent of cyclization can be noted by analyzing for the tertiary amine content, generally referred to as the TAN value of the reaction mixture.

Quaternization of the aforementioned bisimidazolines can be carried out in a conventional manner. Generally, it is desirable to conduct the quaternization reaction by having the bisimidazoline in the form of a concentrated dispersion thereof in an inert organic solvent. Suitable inert solvents include the various lower alkanols and glymes. Isopropanol is especially preferred for this purpose. The inert solvents should be anhydrous insofar as the presence of water tends to promote hydrolysis of the imidazoline rings. The quaternization reaction can be carried out by adding a quaternizing agent to a stirred concentrate of the bisimidazoline. The solid contents of the concentrate for effecting this reaction can range from about 50 to 90 weight percent, but more usually is about 65 to 85 percent on a weight basis. Temperatures applicable for this purpose range from room temperature to about 125°C depending upon the volatility characteristics of the inert solvent employed.

A variety of agents are useful for deriving the quaternized products. An exemplary enumeration thereof include: the lower alkyl chlorides and bromides, e.g., methyl chloride; the di-lower alkyl sulfates; ethylene chlorohydrin; epichlorohydrin and benzyl chloride or iodide. The di-lower alkyl sulfates, specifically, dimethylsulfate, represent the preferred quaternizing agents for preparing the quaternary ammonium compounds contemplated herein.

Although the preferred quaternary ammonium compounds of this invention, especially those wherein the quaternizing anion is methyl sulfate, find particular utility in fabric softening applications, other important uses are indicated. For example, these quaternized products can also be advantageously used in rinsing compositions for human hair, as an emulsifier for preparing oil and water emulsions, including bituminous or asphaltic materials, and as an antistatic agent for paper, fabric, polish, etc.

In order to illustrate those skilled in the art how the present invention can be practiced and utilized, the following working examples are given. As indicated, these examples are set forth solely for the purpose of illustrating the best mode contemplated for carrying out the present invention. Therefore, any enumeration of details contained therein should not necessarily be interpreted as a limitation of the invention. The only limitation intended are those expressed in the appended claims. All parts are by weight unless otherwise stated.

**EXAMPLE I**

Into a suitable reaction vessel equipped with a stirrer and thermometer were charged 146.24 parts (1 mole) of triethylene tetramine and 574 parts (0.667 mole) of bleached soft tallow. With stirring, the reaction mixture was heated at 150°C with a nitrogen sparge for 3 hours to form the polyamido-amine condensation product. Following this reaction period, the apparent molecular weight was 877 and little unreacted triglyceride was indicated by infrared analysis. The di-amido-amine was then heated to 160°-195°C at 15 mm Hg and glycerine and water were removed over a 2-hour period until the tertiary amine content (TAN) of the cyclization product was in excess of 90 weight percent. The resultant bisimidazoline product was thereupon cooled to 65°C and 590 parts thereof (0.734 mole) was dissolved in 255 parts of isopropanol. Dimethylsulfate in the amount of 185 parts (1.468 moles) was added at 65°-75°C until the free amine content was reduced to less than 1 weight percent. The quaternized product was bleached observing conventional procedure therefore, and the solids adjusted to 75 weight percent with added isopropanol.

**EXAMPLE II**

The concentrate (75 wt. percent solids) of Example I in the amount of 33.3 parts was melted until completely clear and thereupon slowly added to 466.7 parts of hot tap water (120°F) with good agitation. The resultant dilute dispersion containing about five percent solids on a weight basis was crystal clear in appearance after cooling to room temperature. Conventional softening, rewet and storage stability tests, details of which and the results obtained are described as follows.

An eight lb. dry load of fabric consisting of four desized white cotton-dacron sheets and four desized
white cotton towels was placed in a household top loading washer with 35g of a commercial heavy duty detergent. The fabric load was washed in the regular warm water wash cycle, and a sufficient amount of the diluted softener solution was added at the commencement of the rinse cycle to provide 0.083 weight percent active softener based on the weight of the fabric. Following the rinse cycle, the wash load was removed and line dried at room temperature for 24 hours. The treated fabrics were then panel rated using an arbitrary scale of 1–4, in which 1 represents the rating assigned to untreated fabric and the value 4 represents the softest rating; that is, the softness associated with the test fabric treated three times with 0.3 weight percent based on cloth using dimethyl distearoyl ammonium chloride as the softener. In accordance with this procedure, the softener product of Example I were assigned ratings of 2.8 to 3.3. By comparison, commercial softeners usually give ratings in the range of 2.5 to 3. Evaluation of the softener of Example I as a wash cycle softener following the procedure outlined above but employing a concentration of 0.14 weight percent softener based on the fabric weight likewise showed the softener product to be excellent for this application. Ratings for such application were from 2.5 to 3.0.

Rewetting was evaluated using a standard wicking test. Swatches (4 in. x 2 in.) were cut from the softened towels and were suspended such that the edge was barely submerged in a dyed water solution. The water solution was permitted to migrate up the swatch for a period of 6 minutes. The extent of migration was then measured in millimeters. Readings for untreated towel samples averaged 75mm whereas towels treated with dimethyl distearoyl ammonium chloride gave readings in the order of 20mm (0.083 weight percent in rinse cycle) and 5mm (0.14 weight percent in wash cycle). In comparison, the softener product of Example I gave readings of 48mm (0.083 weight percent in rinse cycle) and 45mm (0.14 weight percent in the wash cycle).

In addition to the 5 weight percent active dispersion, other dispersions containing 1, 2, 3, 7, 10, and 12 weight percent active were prepared in the manner described above. All solutions were crystal clear and were stable to the extent of exhibiting no splitting or separation after 4 weeks at 70º and 105ºF.

EXAMPLE III

Into a suitable reaction vessel equipped as in Example I were charged 170 parts (1.16 moles) of triethylenetetramine and 580 parts (0.667 mole) of refined soybean oil. With stirring the mixture was heated to 150ºC with a nitrogen sparge for three hours to form the polyamido-amine condensation product. Following this reaction period, the apparent molecular weight was 750 and essentially no unreacted triglyceride was indicated by infra-red analysis. The diamidodiamine was then heated to 160º to 195ºC at 15mm Hg whereupon glycerine water were removed over a two-hour period until the tertiary amine content of the cyclization product was in excess of 85 weight percent. The resultant bisimidazole product was cooled to 65ºC and 600 parts thereof (0.734 mole) were dissolved in 255 parts of isopropanol. Dimethylsulfate in the amount of 185 parts (1.468 moles) was added at 65º to 75ºC until the free amine content dropped to less than 2 weight percent. The quaternized product was bleached observing a conventional procedure and the solids adjusted to 75 weight percent with added isopropanol. The resulting light colored product when following the procedure outlined in Example II gave dilute dispersions at 1–5 wt. percent having a crystal clear appearance. The softener when used at a 0.083 weight percent active level based on the weight of fabric (desized towels) in the rinse cycle gave softening ratings of 2.5 to 3.0.

EXAMPLE IV

Triethylenetetramine in the amount of 150 parts (1.02 moles) was reacted with 440 parts (0.667 mole) of refined coconut oil following the procedure outlined in Example I. The resulting diococ bisimidazole in the amount of 504 parts (0.75 mole) was reacted with 189 parts (1.5 moles) of dimethyl sulfate at 65º to 75ºC until the free amine content dropped to less than 1 weight percent. Upon diluting with water in accordance with the method described in Example II, a 5 weight percent dispersion of the quaternized product exhibited crystal clear clarity. The product possessed good foaming characteristics and was found to be substantive to human hair.

EXAMPLE V

In accordance with the procedure of Example I, tetraethylenepentamine in the amount of 189.24 parts (1 mole) was reacted with 860 parts (1 mole) of bleached soft tallow at 150ºC for 3 hours to provide the trialkyl amidoamine. Following this reaction, the apparent molecular weight was 1105, and infrared analysis indicated a minimal amount of unreacted triglyceride. The triamidoamine was heated to 160º to 195ºC at 15mm Hg whereupon glycerine and water were removed over a 2-hour period until the tertiary amine content was in excess of 90 percent. The resultant bisimidazole in the amount of 977 parts (1 mole) was dissolved in 350 parts isopropanol and reacted with 152 parts (2 moles) of dimethyl sulfate at 65º to 75ºC until the free amine content dropped to less than 2 weight percent. The quaternized product was bleached observing a conventional procedure therefore; and the solids adjusted to 75 weight percent with added isopropanol. The resultant concentrate provided a 2, 3, and 5 weight percent stable dispersions exhibiting crystal clear clarity.

What is claimed is:

1. A quaternary ammonium compound having the formula:

   ![Formula Image]

   wherein R₁ is a C₆–C₂₀ hydrocarbyl group; n is an integer of from 0–4; R₂ is lower alkyl; R is a C₃–C₆ alkylene group; A represents hydrogen or an acyl group of the formula R₃C (O) - in which R₃ has the meaning as aforesaid; and X represents a chloro or a lower alkyl sulfate anion.

2. A compound in accordance with claim 1 wherein R is ethylene.

3. A compound in accordance with claim 2 wherein n is 1.
4. A compound in accordance with claim 3 wherein A is hydrogen.

5. A compound in accordance with claim 3 wherein A is said acyl group.

6. A compound in accordance with claim 2 wherein n is 0.

7. A compound in accordance with claim 5 wherein R<sub>1</sub> represents the hydrocarbyl residues of the carboxyl moiety of tallow fatty acids.

8. A compound in accordance with claim 6 wherein R<sub>1</sub> represents the hydrocarbyl residues of the carboxyl moiety of tallow fatty acids.

9. A compound in accordance with claim 6 wherein R<sub>1</sub> represents the hydrocarbyl residues of the carboxyl moiety of coconut fatty acids.

10. A compound in accordance with claim 6 wherein R<sub>1</sub> represents the hydrocarbyl residues of the carboxyl group moiety of soybean fatty acids.

11. A compound in accordance with claim 7 wherein X represents a lower alkyl sulfate anion.

12. A compound in accordance with claim 8 wherein X represents a lower alkyl sulfate anion.

13. A compound in accordance with claim 11 wherein R<sub>2</sub> is methyl and X is corresponding a methyl sulfate anion.

14. A compound in accordance with claim 12 wherein R<sub>2</sub> is methyl and X is correspondingly a methyl sulfate anion.

* * * * *
UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,855,235
DATED : December 17, 1974
INVENTOR(S) : Robert B. McConnell

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

The formula appearing in Claim 1 at lines 50-58 should read as follows:

\[ \begin{align*}
R_1 & \quad R_2 \\
N & \quad R(NR)_n \quad N \quad X^- \\
R_1-C & \quad CH_2 \quad A \quad CH_2 \quad C-R_1 \\
\end{align*} \]

The formula in column 1 at lines 61-69 should read as follows:

\[ \begin{align*}
R_1 & \quad R_1 \\
N & \quad R(NA)_{n} \quad N \quad N \\
CH_2 & \quad CH_2 \quad CH_2 \\
\end{align*} \]

Column 2, line 3, the formula reading "R1-C-" should read \[ \begin{align*} \]
--- R1-C- ---.

This certificate supersedes Certificate of Correction issued March 11, 1975.

Signed and Sealed this
nineteenth Day of August 1975

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,855,235 Dated October 15, 1974

Inventor(s) Robert B. McConnell

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

The formula appearing in Claim 1 at lines 50-58 should read as shown below:

The formula in column 1 at lines 61-69 should read as shown below:

Column 2, line 3, the formula reading R₁-C- should read 0
-- R₁-C-- .

Signed and sealed this 11 day of March 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks