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(54) **Biodegradable fabric softeners derived from aspartic acid or glutaminic acid.**

(57) Stable aqueous dispersions are described which display a fabric softening action and contain a biodegradable cationic nitrogen compound. The anion of the compound is the anion of a water-soluble organic Bronstedt acid. The acid is present in an amount more than equivalent to the amount of the nitrogen compound. The cationic nitrogen is obtained from an amine which is prepared from an unsaturated dicarboxylic ester e.g. ditallow maleate and an amine e.g. dimethyl amine.

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The invention relates to an aqueous dispersion of a compound derived from an aliphatic aminodicarboxylic acid. More particularly, the invention relates to dispersions for use as fabric softening agents.

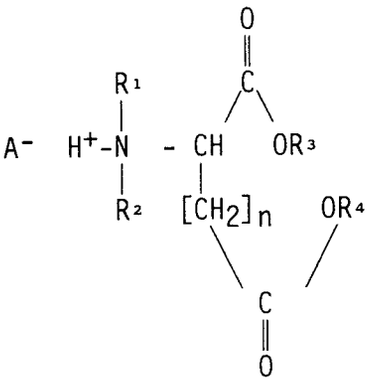
Fabric softeners are generally used to render textiles soft to the touch after a laundry treatment and are incorporated into commercial laundry products such as detergents, rinsing agents, and laundry drying agents. Representative commercial fabric softeners are, e.g., dimethyl distearyl ammonium chloride and 1-methyl-2-tallow-3-tallowamidoethyl imidazoline methosulphate. However, the known fabric softeners have no or only very slow biodegradability and their primarily domestic widescale use is attended with large amounts of them entering, via the sewerage system, the city waste water and complicating its purification.

Due to this behaviour, there is need for novel fabric softening agents which are more readily biodegradable. Moreover, neither these agents nor their (biological) degradation products should exhibit any toxic properties.

A dispersion of the type mentioned in the opening paragraph is known from US Patent Specification No. 4 026 915, which publication is hereby incorporated by reference into the present text for all purposes. The fabric softening compounds described in US 4 026 915 are diesters derived from aspartic acid and characterised in that there is linked to the amino group of the aspartic acid a second amino substituent made up of an organic tertiary amine. Said tertiary amine can be converted into a quaternary ammonium compound or a salt, thus giving a fabric softening agent. These fabric softeners are not sufficiently biodegradable, however.

The invention has for its object to provide compounds which are suitable for use as fabric softeners and exhibit sufficient biodegradability.

Now an aqueous dispersion of the type mentioned in the opening paragraph has been found, in which the compound derived from an aliphatic aminodicarboxylic acid is a cationic nitrogen compound satisfying the following formula:



wherein n equals 1 or 2, R^1 and R^2 may be the same or different and represent hydrogen, alkyl or alkenyl, and R^3 and R^4 may be the same or different and represent alkyl or alkenyl, such that at least 2 of the groups R^1 - R^4 contain 8-24 carbon atoms, at least one of the groups R^1 - R^4 contains 1-4 carbon atoms, and wherein A^- is the anion of a water-soluble organic Bronstedt acid, with the proviso that the acid is present in an amount more than equivalent to the amount of nitrogen compound.

The fabric softening action displayed by the present dispersions is surprising, the more so because the aforementioned US patent specification presupposes that compounds of the described type without the second amino group, the organic tertiary amine substituent, are not suitable to be used as a fabric softening agent.

However, the present invention makes it possible to provide dispersions capable of rendering laundry soft to the touch which are based on amino-substituted aliphatic dicarboxylic acids of little harmfulness to the environment. In this case using more acid than is needed to reach the equivalence point has been found to be a must; an even more satisfactory fabric softening effect is obtained by the use of dispersions according to the present invention, in which the acid is present in at least twice the amount equivalent to the amount of amine.

The present dispersions can be used as fabric softeners which are added separately to the laundry in the washing machine during the rinse cycle. Generally during this rinse the nitrogen compound will be present in a concentration of about 0,5 to 3 g/kg washload. In this respect the invention also relates to a stable aqueous dispersion of the known type mentioned in the opening paragraph, which is characterised in that the compound derived from an aliphatic aminodicarboxylic acid is a cationic nitrogen compound according to the formula given above and the Bronstedt acid is a water-soluble organic acid, the acid being added in such an amount that a dispersion diluted with mains water

which contains 0,5-30 wt.% of nitrogen compound will have a pH below the value corresponding to the molar equivalence point of the nitrogen compound and the acid. Such a dispersion offers the assurance that there will not be any problem if a portion of the acid is inadvertently used up during the rinse cycle, e.g. as a result of scale formation on the heating elements and machine parts or because of residual detergent not removed by rinsing.

Such a dispersion will usually have a pH of less than 5 in the concentrated form. Especially favourable results are obtained if the nitrogen compound and the carboxylic acid are present in such amounts that the concentrated dispersion will have a pH in the range of 1,5-3.

The nitrogen compounds which can be employed with advantage in the present invention are based on aspartic acid and/or glutaminic acid. Preference is given to compounds based on aspartic acid, notably because of their favourable synthetic accessibility. The alkyl or alkenyl groups having 8-24 carbon atoms are preferably incorporated at the R^3 and R^4 positions, the alkyl or alkenyl groups having 1-4 carbon atoms at the R^1 and R^2 positions. With respect to fabric softening action preference is given to the groups R^3 and R^4 being derived from hardened fats (with saturated aliphatic carbon chains). Most suitable by far are diesters according to the invention in which the ester groups R^3 and R^4 are made up of saturated C_{16-18} chains, a fine example being hydrogenated tallow.

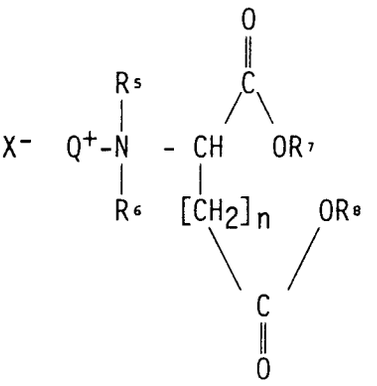
The particle size, viscosity, and storage stability of the dispersions according to the invention are affected by the nature of the acid.

For environmental reasons preference is given to citric acid, malic acid, glycolic acid, and lactic acid, these being the most environment-friendly acids due to their low toxicity, favourable biodegradability, and low aquatoxicity. The acid held to be most suitable in this respect is citric acid.

The invention also provides for the use of a mixture of acids. This is not only the case when a combination of properties is advisable, but also because the use of different acids makes it possible to set the viscosity and the degree of acidity of the dispersions as desired.

In addition to being affected by the nature of the acid employed, the particle size, viscosity, and storage stability of the dispersions according to the present invention can be affected by means of dispersing agents, preferably ethoxylated fatty amines and fatty alcohols. Examples of such dispersing agents are those available under Akzo Chemicals registered trade mark names Ethomeen and Elfapur.

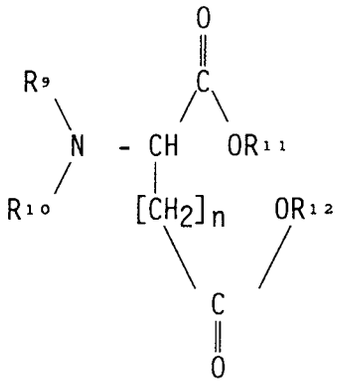
The invention further relates to fabric softening agents comprising a quaternary ammonium compound derived from aspartic and/or glutaminic diesters. The quaternary ammonium compounds according to the present invention satisfy the following formula:



wherein n equals 1 or 2, R^5 - R^8 may be the same or different and represent alkyl or alkenyl, such that at least two of these groups contain 8-24 carbon atoms and at least one of these groups contains 1-4 carbon atoms, Q is an alkyl or hydroxy alkyl group containing 1-6 carbon atoms, and X^- is an anion.

Quaternary ammonium compounds are known in themselves in the field of fabric softeners and no further elucidation is required for the skilled man. It is preferred that Q is methyl and X^- is a halide ion, preferentially Cl^-, or $CH_3SO_4^-$. Unlike the compounds known from US 4 026 915, the quaternary ammonium compounds according to the present invention are readily biodegradable. Also for the quaternary ammonium compounds it holds that the aforementioned prejudice set forth in said US patent specification is not likely to encourage the skilled man to employ the present simple aspartic or glutaminic acid derivatives in fabric softening agents.

The invention further relates to compounds which are favoured for use in fabric softening compositions and satisfy the following formula:



wherein n equals 1 or 2, R^9 and R^{10} may be the same or different and represent hydrogen, an alkyl or alkenyl group having 1-4 carbon atoms, and R^{11} and R^{12} may be the same or different and represent an alkyl or alkenyl group having 8-24 carbon atoms.

These preferred embodiments can be employed in fabric softeners in the manners indicated hereinbefore, i.e. as a salt or in the quaternized form. In addition to these specific tertiary aminodicarboxylic acids having a favourable fabric softening action, the compounds have the advantage of more ready biodegradability as compared with compounds according to the aforementioned US 4,026,915. Also for reasons of synthetic accessibility further preference is given to dimethylamino dihydrogenated tallow aspartate.

The preparation of amino compounds which can be used as starting material for the cationic nitrogen compounds according to the present invention may, int. al., be carried out by making use of an unsaturated dicarboxylic ester, e.g. dihydrogenated tallow maleate, and then reacting it with an amine. Such a preparative process as well as the preparation of the diester may be carried out analogous to the description in the aforementioned US patent specification.

The invention will be further illustrated with reference to the following unlimitative examples.

Example 1

To a solution of 120 g (0,2 moles) of dihydrogenated tallow maleate, which was obtained from maleic anhydride and hydrogenated tallow alcohol (Loxiol G53 ex Henkel), in one liter of THF were charged at room temperature 45 g (0,4 moles) of a 40% aqueous solution of dimethylamine. The solvent and excess of dimethylamine were evaporated at reduced pressure, the product being obtained as a white solid. No maleic or fumaric ester, the latter being formed during the reaction, could be determined by ^{1}H-NMR spectroscopic measurements.

The same product may also be obtained without solvent by reacting 689 g (1,15 moles) of molten dihydrogenated tallow maleate and 91 ml (1,38 moles) of gaseous dimethylamine in the autoclave at a temperature of 110°-120°C. Decreasing the dimethylamine to the equimolar amount caused a decrease of the base number by 3%.

The N,N-dimethyl dihydrogenated tallow aspartate was converted to its cationic form through the addition of 5 wt.% of the N,N-dimethyl dihydrogenated tallow aspartate to a solution of 5 wt.% of citric acid monohydrate and 1 wt.% of Elfapur® LM75S in demineralized water heated, with stirring, to 60°C and subsequently cooled, with stirring, to 20°C. The pH value of the undiluted dispersion was 2,1.

The dispersion was found to have favourable fabric softening properties.

Biodegradability was tested in accordance with the EEC/OECD guidelines, using the so-called "Closed Bottle Test". The present cationic nitrogen compound was found to meet the requirements for being designated readily biodegradable, which means biodegradation of at least 60% within 28 days.

Example 2

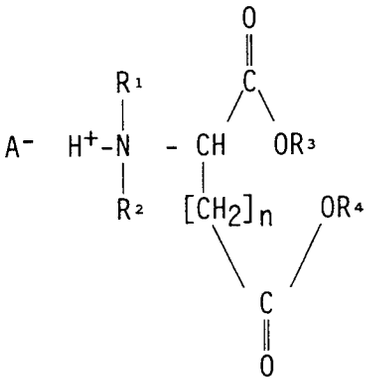
In the known manner a quaternary ammonium compound was prepared from N,N dimethyl dihydrogenated tallow aspartate by reaction with methyl iodide. Using the aforementioned test the quaternary ammonium compound was found to be "readily biodegradable", since 64% of it was found to have been degraded within 28 days.

Comparative Example

In the above-described manner and using methyl iodide-quaternized N-[(3-dimethylamino)-propyl] dihydrogenated tallow aspartate a compound according to US Patent Specification No. 4 026 915 was tested for biodegradability, the result being that after 28 days a mere 18% had been degraded. Continuation of the test showed 39% degradation after 75 days.

Claims

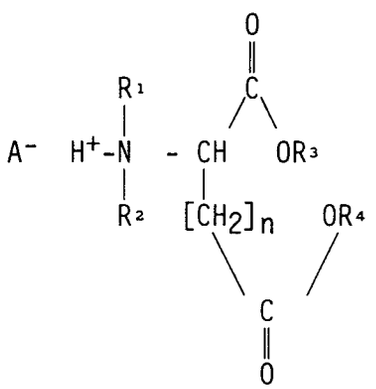
1. A stable aqueous dispersion of a cationic amino compound derived from an aliphatic aminodicarboxylic acid, characterised in that the cationic amino compound satisfies the following formula:



wherein n equals 1 or 2, R^1 and R^2 may be the same or different and represent hydrogen, alkyl or alkenyl, and R^3 and R^4 may be the same or different and represent alkyl or alkenyl, such that at least 2 of the groups R^1 - R^4 contain 8-24 carbon atoms and, in the case of neither R^1 nor R^2 representing hydrogen, at least one of the groups R^1 - R^4 contains 1-4 carbon atoms, and wherein A^- is the anion of a water-soluble organic Bronstedt acid, with the proviso that the acid is present in an amount more than equivalent to the amount of nitrogen compound.

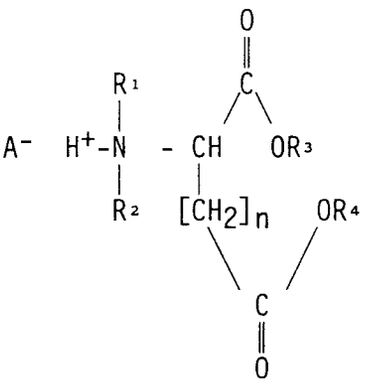
2. A stable aqueous dispersion according to claim 1, characterised in that the acid is present in it in at least twice the equivalent amount of amino compound.

3. A stable aqueous dispersion comprising a cationic amino compound derived from an aliphatic aminodicarboxylic acid, characterised in that the cationic amino compound satisfies the following formula:



wherein n equals 1 or 2, R^1 and R^2 may be the same or different and represent hydrogen, alkyl or alkenyl, and R^3 and R^4 may be the same or different and represent alkyl or alkenyl, such that at least 2 of the groups R^1 - R^4 contain 8-24 carbon atoms and, in the case of neither R^1 nor R^2 representing hydrogen, at least one of the groups R^1 - R^4 contains 1-4 carbon atoms, and wherein A^- is the anion of a water-soluble organic Bronstedt acid, with the proviso that the acid is added in such an amount that a dispersion diluted with mains water which contains 0,5-30 wt.% of amino compound will have a pH below the value corresponding to the molar equivalence point of the amino compound and the acid.

4. A stable aqueous dispersion comprising a cationic amino compound derived from an aliphatic aminodicarboxylic acid, characterised in that the cationic amino compound satisfies the following formula:



wherein n equals 1 or 2, R^1 and R^2 may be the same or different and represent hydrogen, alkyl or alkenyl, and R^3 and R^4 may be the same or different and represent alkyl or alkenyl, such that at least 2 of the groups R^1 - R^4 contain 8-24 carbon atoms and, in the case of neither R^1 nor R^2 representing hydrogen, at least one of the groups R^1 - R^4 contains 1-4 carbon atoms, and wherein A^- is the anion of a water-soluble organic Bronstedt acid, with the proviso that the amino compound and the carboxylic acid are present in such an amount that the dispersion in the concentrated form has a pH of less than 5.

5. A stable aqueous dispersion according to claim 4, characterised in that the pH is in the range of 1,5-3.

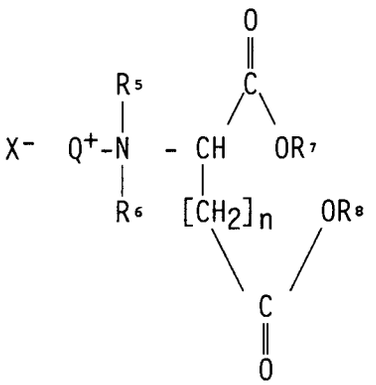
6. A stable aqueous dispersion according to any one of the preceding claims, characterised in that the cationic amino compound is dimethyl dihydrogenated tallow aspartate.

7. A stable aqueous dispersion according to any one of the preceding claims, characterised in that the organic acid is a hydroxycarboxylic acid.

8. A stable aqueous dispersion according to claim 6, characterised in that the hydroxycarboxylic acid is citric acid, malic acid, lactic acid or glycolic acid.

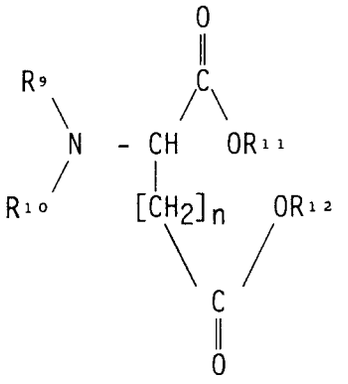
9. A fabric softener comprising an aqueous dispersion according to any one of the preceding claims.

10. A fabric softener comprising a quaternary ammonium compound satisfying the following formula:



wherein n equals 1 or 2, R^5 - R^8 may be the same or different and represent alkyl or alkenyl, such that at least two of these groups contain 8-24 carbon atoms and at least one of these groups contains 1-4 carbon atoms, Q is an alkyl or hydroxy alkyl group containing 1-6 carbon atoms, and X^- is an anion.

11. Use of a compound satisfying the formula:



wherein n equals 1 or 2, R^9 and R^{10} may be the same or different and represent an alkyl or alkenyl group having 1-4 carbon atoms, and R^{11} and R^{12} may be the same or different and represent an alkyl or alkenyl group having 8-24 carbon atoms, in fabric softening compositions.