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(21) International Application Number: PCT/EP91/02178 (22) International Filing Date: 14 November 1991 (14.11.91) (30) Priority data: 9002506 16 November 1990 (16.11.90) NL (71) Applicant (for all designated States except US): AKZO N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL). (72) Inventors; and (75) Inventors/Applicants (for US only) : RÖRIG, Hans [DE/DE]; Am Olligsmar 26, D-5161 Merzenich (DE). WEUSTE, Burkhard [DE/DE]; Sienhardtstrasse 38, D-5270 Gummersbach (DE). (74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo N.V., Velperweg 76, Postbus 9300, NL-6800 Arnhem (NL).		(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US. Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: BIODEGRADABLE FABRIC SOFTENERS (57) Abstract The invention pertains to biodegradable fabric softeners based on selected amines which, in protonated form, exhibit an unexpectedly favourable softening action. The selected amines essentially contain ester-groups, and preferably are diester amines.		

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BIODEGRADABLE FABRIC SOFTENERS

5 The present invention relates to fabric softening agents, more particularly amine compounds containing one or more long-chain alkyl or alkenyl groups.

10 Fabric softeners are commonly 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 commercially available fabric softeners include dimethyl distearyl ammonium chloride and 1-methyl-2-tallowalkyl-3-tallowamido-ethyl imidazolinium methosulphate. These known fabric softeners display a serious drawback in that they have no or only very slow biodegradability, whereas their
15 primarily domestic wide-scale use is attended with large amounts of them ending up, via the sewerage system, in the city waste water and complicating its purification.

20 Consequently, there is need for novel fabric softening agents which are more readily biodegradable. Moreover, neither these agents nor their biological degradation products must exhibit any toxic properties. The current invention has for an object to meet this need by providing fabric softeners on the basis of amine compounds.

25 Fabric softeners comprising amine compounds have been described before.

30 Canadian Patent No. 1 164 470 discloses the use of a wide range of protonated amines as additives for a number of formulations, including fabric softener formulations. No indication is given as to whether any of the disclosed compounds could themselves exhibit softening activity.

5 In EP A 281 975 a wide range of amines is disclosed which act as a softening-activity imparting ingredient if formulated together with a carboxylic acid having of from 1 to 24 carbon atoms. No indication is given as to whether any of the disclosed compounds would be biodegradable.

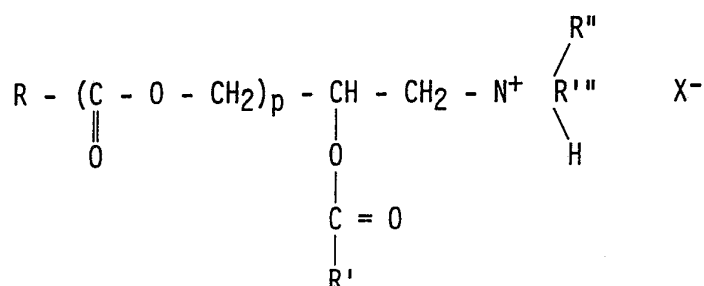
10 In EP-A-417 987, published after the priority date to which the instant invention is entitled, certain amines are disclosed to be effective softeners if formulated together with a pH adjusting agent under certain conditions. The disclosure illustrates one major problem confronting the person of ordinary skill in the art who intends to provide amine-based softeners: amine-containing fabric softener
15 compositions often do not soften well.

EP 293 953 pertains to fabric softeners comprising quaternary ammonium fabric softeners containing a single ester group. The disclosed quaternary ammonium compounds are stated to be biodegradable, but
20 further improvement in this respect is desired. The disclosure does not pertain to the problem of formulating effective, biodegradable softeners based on amines.

DE-PS-27 28 841 discloses fabric softeners based on quaternary
25 ammonium compounds containing two ester moieties. The disclosure does not pertain to biodegradability, nor does it address the aforementioned problem of formulating effective softeners based on amine compounds.

30 It has now been found that a select group of amine compounds display such unexpectedly favourable characteristics as to make them more efficient fabric softeners than other amines, as well as more readily biodegradable.

Therefore, the present invention provides a biodegradable fabric softening agent which comprises as essential constituent an ester group-containing cationic nitrogen compound of the formula 1:



wherein R represents an alkyl or alkenyl group having 7-22 carbon atoms.

R' represents an alkyl or alkenyl group having 7-21 carbon atoms.

R" and R'" may be the same or different and represent an alkyl or hydroxyalkyl group having 1-6 carbon atoms.

p equals 0 or 1, and

X⁻ represents an anion.

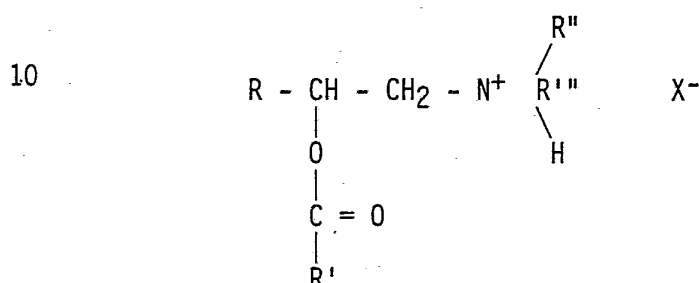
The amine is required to be protonated to provide a favourable softening action. This is generally effected by employing the amine in fabric softening compositions having a low enough pH to have the amine present in the rinse in the protonated form. This means that the amine is present in softener compositions in conjunction with an acid. Hence the counterion X^- is an acid radical.

It should be noted that, surprisingly, an effective softener is provided by the instant select group of protonated amines without additional steps being required. This is not to say that additional steps, such as described in EP 417 987 referred to above, will negatively affect the performance of the instant softening agents. On the contrary, if the steps according to EP 417 987 are applied to the amines according to the present invention, an even better softening

performance is attained as compared with Armeen[®]M2HT. Rather, it is stressed that no additional steps being required shows the unexpected and unique performance of the instant selected amines.

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According to a preferred embodiment of the present invention the cationic nitrogen compound is of the formula 2:

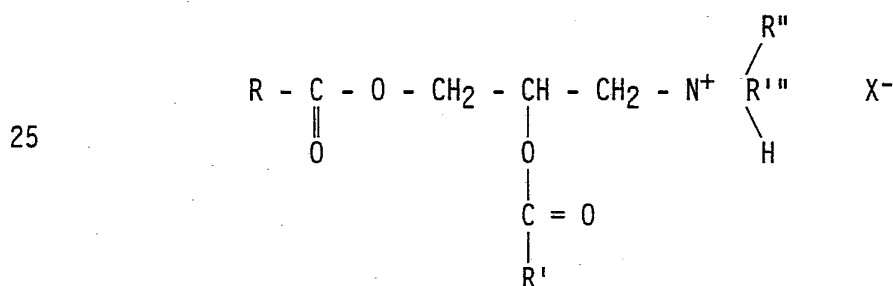


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wherein R represents an alkyl or alkenyl group having 8-22 carbon atoms and R', R'', R''', and X⁻ may have the above-disclosed meanings.

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According to a further preferred embodiment of the present invention the cationic nitrogen compound is of the formula 3:



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wherein R and R' represent an alkyl or alkenyl group having 8-22 carbon atoms and R'', R''', and X⁻ may have the above-disclosed meanings.

The amine compounds of the latter formula display a further advantage in that they are more readily biodegradable than Armeen[®]M2HT disclosed

in EP-A-417 987, particularly if R" and R'" are methyl and R and R' are C_{15/17} saturated hydrocarbon.

5 In the above formulae R and R' preferably represent essentially linear alkyl or alkenyl groups that may be derived from fatty acids or mixtures thereof. In actual practice it is alk(en)yl groups usually derived from natural fatty acid mixtures, such as tallow alkyl, hydrogenated tallow alkyl (H-tallow alkyl), and coco alkyl, that are
10 made use of. These groups are also preferred for use in the biodegradable fabric softeners according to the present invention on account of their easy availability at a low price.

The nature of the short-chain (hydroxy)alkyl group is essentially
15 determined by the starting material. In actual practice preference is given to methyl and 2-hydroxyethyl.

As indicated above, the proton in the protonated amine may be hydrogen derived from the acid fabric softener medium.

20 The counterion X⁻ is an acid radical, preferably of an organic carboxylic acid and more particularly of a hydroxycarboxylic acid. Most suitable are citric acid, malic acid, and glycolic acid. Of course, acids are well-known to the person of ordinary skill in the art, and need no further elucidation here. To affect protonation of
25 the instant amines the acid may simply be mixed with an equivalent amount of amine. Complicated melting processes, such as disclosed in EP-A-281 975, are not required.

30 The present cationic nitrogen compounds can be prepared in the manner known for the preparation of analogous compounds. In the examples which will follow the preparation of a representative cationic nitrogen compound according to the present invention is described in detail, and the remaining biodegradable fabric softening agents

according to the present invention are directly accessible to the skilled man through adaptation of the starting substances concerned.

5 The manner in which the present biodegradable fabric softening agent is applied is the same as for the conventional, now commercially available fabric softeners. The usual possibilities in this respect are either using the agent in admixture with detergent, or adding it separately, i.e. during the rinse-cycle as a rinsing agent or else in
10 the dryer. The instant softening agents are particularly advantageous as rinse-cycle added softeners.

The fabric softening action envisaged and actualised here is at least the same as for the conventional quaternary ammonium fabric softeners.
15 Inevitably, via the rinsing solution a portion of the fabric softener will end up in the waste water, where, because of the present invention, there will be less harm to the environment as a result of accelerated biodegradability.

20 The present biodegradable fabric softening agents were tested for their fabric softening performance and found to be comparable with dimethyl dihardened tallow ammonium chloride, distearyl ammonium chloride and 1-methyl-2-tallowalkyl-3-tallowamido-ethyl imidazolinium methosulphate. In the test towels treated with the fabric softeners in
25 question were line dried for 24 hours and then cut up into STRIPS of 10 x 20 cm². A test panel evaluated the softening action as compared with that of the standard test detergents (IEC), whereupon the observational data was statistically processed in accordance with DIN standard 10954.

30 The present quaternary ammonium compounds were tested for biodegradability in accordance with the EEC/OECD guidelines OECD 301D "closed bottle test". In this experiment a test compound is added to an aqueous solution of mineral salts and exposed for 28 days under

aerobic conditions to a relatively small number of micro-organisms. The formal test regulations were departed from on the following minor issues:

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- the inoculum was taken from an apparatus containing activated sludge preconditioned in accordance with proposed amendments to the EEC guidelines;
- ammonium chloride was not included in the medium to avoid

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nitrification;

The dissolved oxygen concentrations were determined electrochemically using an oxygen electrode (WTW Trioxmatic EO 200) and an oxygen gauge (WTW OXI 530), and biodegradability was calculated as the ratio of biological oxygen demand (BOD) to theoretical oxygen demand (ThOD):

15

BOD/ThOD.
Compared with the aforementioned commercially available fabric softeners a significantly accelerated biodegradability was observed.

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

Example 1

544 g (2 moles) of hydrogenated tallow fatty acid were melted and added to 130 g (1.1 mole) of 3-dimethylamino-1,2-propane diol in a 1 l 3-necked round bottom flask provided with a temperature control unit and a rectification apparatus. The homogeneous mixture was stirred for 4 hours at 190°C and 100 mbar and additionally for 2 hours at 190°C and 5 mbar.

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The conversion was monitored with the aid of either TLC or GC. After 6 hours, the composition of the product was as follows:
90.4% of diester amine, 4.9% of monoester amine, and 4.7% of free fatty acid.

The diesteramine was converted into the corresponding cationic nitrogen compound by protonation with citric acid monohydrate. Said protonation was carried through by adding to water, with stirring, 5 wt% of the diester amine and the equivalent amount of 1.66 wt% of citric acid monohydrate. In the case of the embodiment using excess acid 5 wt% of the diester amine and 5 wt% of citric acid monohydrate were added to water. The addition of the diester amine to water resulted in a stable dispersion.

Example 2

272 g (1 mole) of hydrogenated tallow fatty acid were melted and added to 130 g (1.1 mole) of 3-dimethylamino-1,2-propane diol in a manner analogous to that described in Example 1. After 2.5 hours the reaction was discontinued. The product contained 65% of monoester amine.

The monoesteramine was converted into the corresponding cationic nitrogen compound by protonation with citric acid monohydrate. Said protonation was carried through by adding to water, with stirring, 5 wt% of the monoester amine and the equivalent amount of 2.8 wt% of citric acid monohydrate. In the case of the embodiment using excess acid 5 wt% of the monoester amine and 5 wt% of citric acid monohydrate were added to water. The addition of the monoester amine to water resulted in a clear solution.

The results attained with the protonated amine softeners of the instant invention can be summarized with reference to softening performance and biodegradability as follows.

Softening performance is indicated as follows:

- unsatisfactory
- + satisfactory
- 5 ++ good
- +++ excellent

Biodegradability is indicated by means of the percentage of degradation after 28 days. A compound is considered to be "readily biodegradable" if biodegradation is $\geq 60\%$. Further improved biodegradability is shown if the percentage is over 70%, which may be regarded as ultimate biodegradation. The margin of error in these tests usually is 10%.

15 The following compounds in accordance with the formula given in claim 1 were used:

A: R and R' are saturated C_{15/17} hydrocarbon

R" = R'" is methyl

20 p = 1

B: R and R' are saturated C_{15/17} hydrocarbon

R" = R'" is ethyl

p = 1

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C: R = saturated C_{15/C17} hydrocarbon

R' = hydrogen

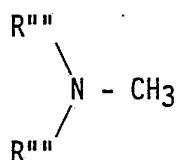
R" = R'" is methyl

p = 1

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To compare the amines according to the instant invention with amines not in accordance with the invention, Armeen[®]M2HT was used. This satisfies the formula

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in which R''' is a hardened tallow alkyl radical.

Results were as follows:

10	Compound	Protonated Amine Formulation	Softening	Biodegradability of pure amine
	A	Citric acid, equiv. amt.	++	78
	A	Citric acid, excess amt.	+++	
15	B	Citric acid, equiv. amt.	+	63
	B	Citric acid, excess amt.	++	
	C	Citric acid, equiv. amt.	++	59
	C	Citric acid, excess amt.	++	
20	Armeen®M2HT	Citric acid, equiv. amt.	-	60
	Armeen®M2HT	Citric acid, excess amt.	++	

From the above table it is apparent that protonated amines according to the present invention are favourable biodegradable softeners. It is also apparent that protonated amine formulations not in accordance with the present invention may make viable softeners but will not exhibit said surprising softening effect without additional steps.

In acute toxicity tests with Algae, Daphnia, and Fish, low toxicity values were established for amine compounds according to the invention, i.e. LC 50 and EC 50 values, respectively, above at least 1 ppm. For the above-identified preferred diester amine (A) these values were above 10 ppm. Since these tests were carried out in

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accordance with the procedures known to the person of ordinary skill in the relevant art, no description needs to be given here.

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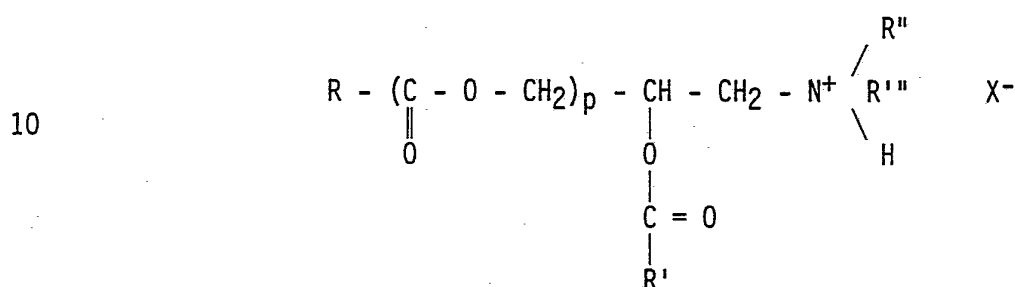
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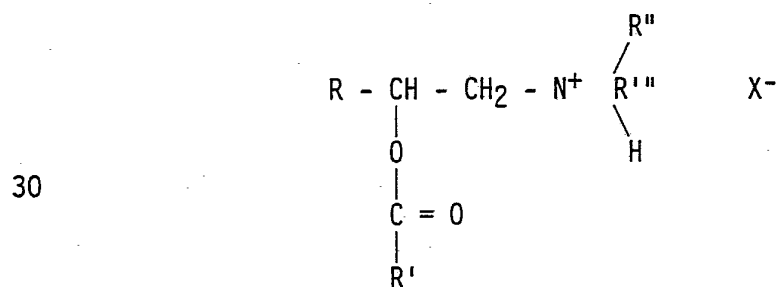
Claims

1. A biodegradable fabric softening agent which comprises as essential constituent an ester group-containing cationic nitrogen compound of the formula 1:



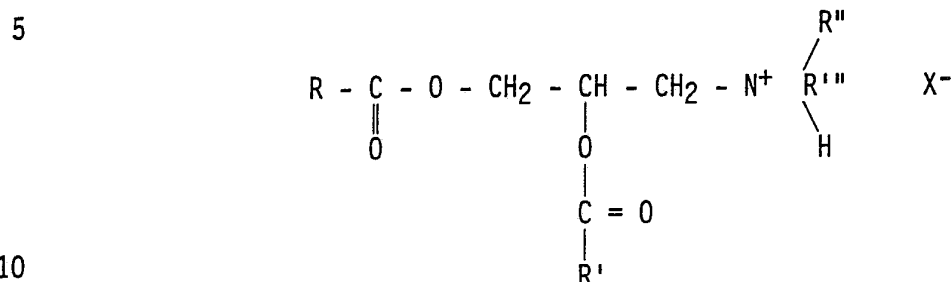
- wherein R represents an alkyl or alkenyl group having 7-22 carbon atoms,
 R' represents an alkyl or alkenyl group having 7-21 carbon atoms,
 R'' and R''' may be the same or different and represent an alkyl or hydroxyalkyl group having 1-6 carbon atoms,
 p equals 0 or 1, and
 X⁻ represents an anion.

2. A fabric softening agent according to claim 1, characterised in that the cationic nitrogen compound is of the formula 2:



- wherein R represents an alkyl or alkenyl group having 8-22 carbon atoms and R', R'', R''', and X⁻ may have the meanings disclosed in claim 1.

3. A fabric softening agent according to claim 1, characterised in that the cationic nitrogen compound is of the formula 3:



wherein R and R' represent an alkyl or alkenyl group having 7-14 carbon atoms and R'', R''', and X⁻ may have the meanings disclosed in claim 1.

- 15
4. A fabric softening agent according to any one of the claims 1-2, characterised in that R represents one or more alkyl groups having 12-18 carbon atoms, more particularly H-tallow alkyl or coco-alkyl.
- 20
5. A fabric softening agent according to any one of the claims 1-2, characterised in that R' represents one or more alkyl groups having 11-17 carbon atoms, more particularly derived from H-tallow acyl or coco-acyl.
- 25
6. A fabric softening agent according to claim 1 or 2, characterised in that R' represents one or more alkyl groups having 11-13 carbon atoms, more particularly derived from coco-acyl.
- 30
7. A fabric softening agent according to any one of the claims 1-3, characterised in that R'' represents a methyl or 2-hydroxyethyl group.
8. A fabric softening agent according to any one of the claims 1-3, characterised in that X⁻ represents citrate.

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9. Protonated (2-H-tallowacyloxy-2-cocoalkylethyl)dimethyl amine.

10. Protonated (2,3-dicocoacyloxypropyl)dimethyl amine.

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11. Use of an ester group-containing cationic nitrogen compound according to any one of the preceding claims as a fabric softening agent for textiles.

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