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(71) Applicant: **UNILEVER PLC**
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ(GB)
(84) **GB**

Applicant: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)
(84) **CH DE ES FR IT LI NL SE**

(72) Inventor: **Evans, Huw, Unilever Research Port Sunlight Lab.**
Quarry Road East, Bebington
Wirral, Merseyside L63 3JW(GB)

(74) Representative: **Stancliffe, Terence Christopher et al**
UNILEVER PLC Patents Division P.O. Box 68
Unilever House
London EC4P 4BQ(GB)

(54) Fabric softening.

(57) A fabric softening composition comprising one or more amine softening materials and one or more pH adjusting agents, wherein the pH of an aqueous liquor obtained by diluting said fabric softening composition to a concentration of 200 ppm of the amine materials has a pH which is equal to or below the pK_a of the amine materials. Preferably the composition is a liquid satisfying the following condition:
$1.5 < pK_a$ (pH adjuster) $< pK_a$ (amine)

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FABRIC SOFTENING

The present invention relates to fabric softening compositions, in particular to fabric softening compositions containing one or more amines as active materials, which are intended for use in the rinse cycle of a fabric washing process.

It is an object of the present invention to formulate fabric softening compositions comprising one or more amines as the active materials. It is a further object of the present invention to provide fabric softening compositions which are environmentally acceptable and which show a good softening performance. One of the problems with amine-containing fabric softener compositions is that they often do not soften as well as conventional softeners containing quaternary ammonium softener materials.

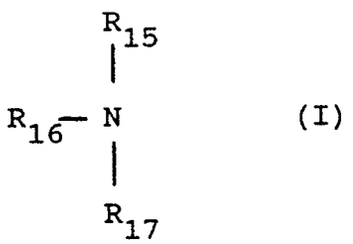
It has now been found that the softening performance of amine containing fabric softener compositions can significantly be improved by carefully controlling the pH of the aqueous rinse liquor for treating the fabrics. The concentration of amine materials in the rinse water will generally be from 30 to 1000 ppm, preferably around 200. It has been found that improved softening can be obtained when the pH of an aqueous rinse liquor comprising the amine softener materials at a concentration of 200 ppm is equal to or below the pK_a of the amine.

Accordingly, the present invention relates to a fabric softening composition comprising one or more amine softening materials and one or more pH adjusting agents, wherein the pH of an aqueous liquor obtained by diluting said fabric softening composition to a concentration of 200 ppm of the amine materials has a pH which is equal to or below the pK_a of the amine materials.

The amine material

The term amine softening material as used herein can refer to any amine material which can be used for the softening of fabrics, for example one or more amines of the following formula can be used:

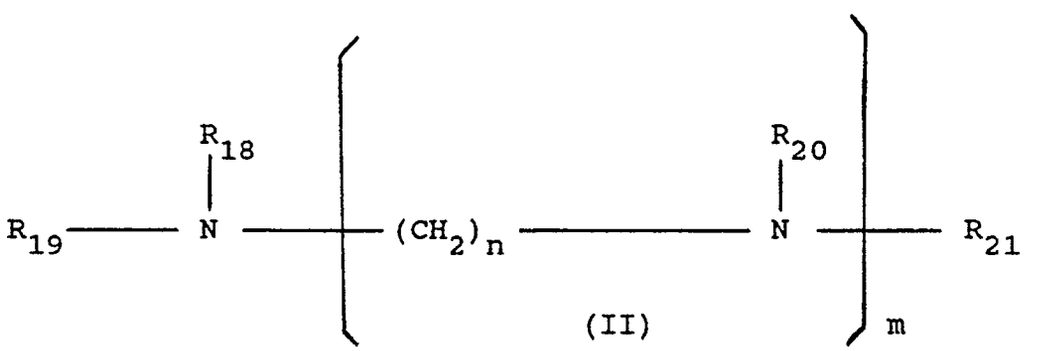
(i) amines of formula



(I)

wherein R_{15}, R_{16} and R_{17} are defined as below;

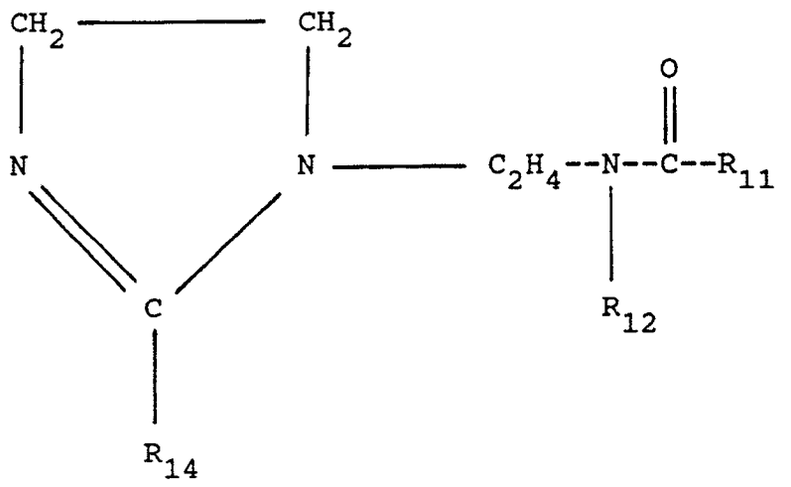
(ii) amines of formula



(II)

wherein R_{18}, R_{19}, R_{20} and R_{21}, m and n are defined as below.

(iii) imidazolines of formula



III

wherein R_{11}, R_{12} and R_{14} are defined as below.

(iv) condensation products formed from the reaction of fatty acids with a polyamine selected from the group consisting of hydroxy alkylalkylenediamines and dialkylenetriamines and mixtures thereof. Suitable materials are disclosed in European Patent Application 199 382 (Procter and Gamble), incorporated herein by reference.

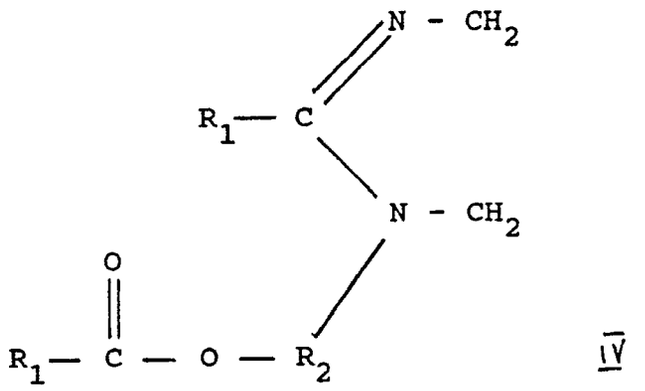
When the amine is of the formula I above, R_{15} is a C_6 to C_{24}, hydrocarbyl group, R_{16} is a C_1 to C_{24} hydrocarbyl group and R_{17} is a C_1 to C_{10} hydrocarbyl group. Suitable amines include those materials wherein both R_{15} and R_{16} are C_6-C_{20} hydrocarbyl with C_{16}-C_{18} being most preferred and with R_{17} as C_{1-3} hydrocarbyl, or R_{15} is an alkyl or alkenyl group with at least 22 carbon atoms and R_{16} and R_{12} are C_{1-3} alkyl.

When the amine is of formula II above, R_{18} is a C_6 to C_{24} hydrocarbyl group, R_{19} and R_{21} are alkoxylated groups of formula $-(CH_2CH_2O)_yH$, where y is within the range from 0 to 6, R_{20} is an alkoxylated group of formula $-(CH_2CH_2O)_zH$ where z is within the range from 0 to 6 and m is an integer within the range from 0 to 6, and is preferably 3. When m is 0, it is preferred that R_{18} is a C_{16} to C_{22} alkyl and that the sum total of z and y is within the range from 1 to 6, more preferably 1 to 3. When m is 1, it is preferred that R_{18} is a C_{16} to C_{22} alkyl and that the sum total of x and y and z is within the range from 3 to 10. n is 1-6, preferably 2.

Representative commercially available materials of this class include Ethomeen (ex Armour) and Ethoduomeen (ex Armour).

When the amine is of formula (III), R_{11} is a hydrocarbyl group containing from 8 to 25 carbon atoms, R_{14} is an hydrocarbyl group containing from 8 to 25 carbon atoms and R_{12} is hydrogen or an hydrocarbyl containing from 1 to 4 carbon atoms and A^- is an anion, preferably a halide, methosulfate or ethosulfate.

Amines of type (iv) are for example substituted imidazoline compounds having the formula IV



IV

where R_1 is an acyclic aliphatic C_{15}-C_{21} hydrocarbon group and R_2 is a divalent C_1-C_3 alkylene group and mixtures thereof.

Preferred amine materials are materials of formula (I), which comprise two long hydrocarbyl groups (C_6-C_{24}) and one short hydrocarbyl group (C_1-C_3). Especially preferred is the use of dihardened tallow methyl

amine, as marketed under the tradename ARMEEN M2HT (Akzo). When the latter material is used the pH of a 200 ppm rinse liquor is preferably 4.5 or less, more preferred less than 3.5.

In this specification the expression hydrocarbyl group refers to alkyl or alkenyl groups optionally substituted or interrupted by functional groups such as -OH, -O-, -CONH, -COO-, etc.

The pK_a value

The pK_a value is a well-known parameter related to the protonation of materials. For a certain amine material the pK_a can be determined by considering the protonation reaction of the amine material:

amine + H^+ -------- amineH^+

The pK_a of the amine is the pH value, at which the amount of unprotonated amine is equal to the amount of protonated amine. A possible method of determining the pK_a of a substance is to determine the titration curve of a 1% dispersion of the material with increasing amounts of acid; the pK_a of the material is the pH value at the midpoint of the steep part of the titration curve.

In table 1, the pK_a value for a number of amine softening materials is given:

TABLE I

AMINE MATERIAL	FORMULA	TRADE NAME	pK_a
methyl dihardened tallow	(i)	Armeen M2HT	4.5
1,2 dihardened tallow oxy dimethyl propane amine	(i)	DTDMPA	5.1

It is preferred to use amine materials having a pK_a of less than 6.5, more preferred less than 5.5, especially preferred between 5.2 and 4.0.

If more than one amine material is present in a composition of the invention, the pK_a value of the amine material should be taken as the weight average pK_a value of the amine mixture.

Liquid products

Compositions of the present invention may take a variety of forms such as liquids, pastes, gels, powders, tablets, flakes etc. Preferably compositions of the present invention are liquids, comprising an aqueous phase. Preferably the water level in such aqueous liquids is from 97 to 20% by weight of the composition, more preferred from 95 to 70%. The level of amine softener materials in products of the invention, especially liquid products of the invention, is preferably more than 1% by weight of the composition, more preferred more than 2%, most preferred more than 3%. Preferably the level of amine softener materials will not exceed 70% by weight of the composition, more preferred the level is less than 30%, especially preferred are compositions comprising from 3 to 20% by weight of amine softener materials.

A problem in the formulation of liquid products according to the invention is that the low pH requirement for the rinse liquor, generally requires high levels of pH adjusting agents in the undiluted product. These high levels of pH adjusting agents, however, often cause the undiluted product to be unstable due to the flocculation of the dispersed amine phase resulting in phase separation. A second object of the present invention is to prevent instability of the undiluted product, while still ensuring that an adequate amount of pH adjusting materials are present.

It has been found that instability of liquid fabric softeners according to the invention can be prevented by ensuring that the pH adjusting agents are predominantly in their unionised form in the undiluted product. Furthermore, the pH of the undiluted product may not be too low for consumer safety. Also the pH adjusting material should have a sufficiently low pK_a to provide the required pH at a 200 ppm concentration of the amine. It has been found that a compromise between these factors can be reached by seleoting a pH adjusting agent, which satisfies the following condition:

$1.5 < pK_a$ (pH adjuster) $< pK_a$ (amine)

More preferably:

$2.0 < pK_a$ (pH adjuster) $< pK_a$(amine)-0.5

Most preferably:

$2.5 < pK_a$ (pH adjuster) $< pK_a$(amine)-1.0

If pH adjusters are used which undergo more than one deprotonation step, then the pK_a (pH adjuster) for use in the above given equations is the lowest pK_a value of the pH adjusting material. For example citric acid has pK_a values of 3.1, 4.8 and 6.4. In the above given equations the value 3.1 is used as the pK_a (citric acid).

If more than one pH adjuster is used then the pK_a value for the mixture of pH adjusters is the weight average pK_a of the mixture of pH adjusting materials.

Other possible methods for increasing the stability of liquid products according to the invention are for example, the use of pH adjusting agents, which are relatively insoluble in the undiluted product, but sufficiently soluble in the rinse liquor, and the use of ingredients which prevent flocculation of the dispersed phase. Examples of suitable deflocculating materials are disclosed in our copending patent application 8919669.5 as filed 31-08-1989 at the British Patent Office.

The pH adjusting agents

Compositions according to the invention also comprise one or more pH adjusting agents. As described above, the pH adjusting agents should provide a certain pH for the rinse water. As soon as the required pH for the rinse water has been determined in line with the teaching as given above, it is believed to be well within the ambit of the skilled person, to select the types and amounts of pH adjusting materials necessary to obtain the required pH. Generally the pH adjusting agents will be acid materials.

When the product of the invention is a liquid product, comprising an aqueous base it is preferred that the pH adjusting materials have a pK_a which is above 1.5, but below the pK_a of the amine. Again it is believed that as soon as the desired pK_a for the pH adjusting agents has been found with help of the above teaching, then it is well within the ambit of the skilled person to select suitable acids and their amounts.

Typical concentrations for the pH adjusting materials in the liquid undiluted products are from 0.1 to 2.0 mole per litre, more preferably from 0.2 to 1.5 mole per litre, especially preferred from 0.25 to 1.0 mole per litre.

Preferred pH adjusting materials have a pK_a of between 2.5 and 3.5. Examples of these materials are p-Aminobenzosulphonic acid, bromoacetic acid, chloroacetic acid, o-chloroacetic acid, alpha chlorobutyric acid, citric acid, dihydroxybenzoic acid, dimethylmalic acid, dimethylmalonic acid, dinicotinic acid, fumaric acid, furancarboxylic acid, iodoacetic acid, lactic acid, malic acid, malonic acid, methyl malonic acid, quinolinic acid, sulfanilic acid and tartaric acid. For environmental reasons the use of tartaric acid, lactic acid, citric acid, malonic acid or mixtures thereof is preferred.

Preferably the pH adjusting materials having a pK_a of between 2.5 and 3.5 are used in combination with amines of formula (i), which comprise two long hydrocarbyl groups (C_6-C_{24}) and one short hydrocarbyl group (C_1-C_3). Especially preferred is the use of these pH adjusting materials in combination with dihardened tallow methyl amine, as marketed under the tradename ARMEEN M2HT (Akzo).

Optional ingredients

Compositions of the present invention may comprise in addition to the above mentioned amine and pH adjusting materials one or more other softener materials selected from cationic, amphoteric and nonionic softening materials. Suitable materials are for example described in EP 239 910 (P&G), US 3 915 865 (STEPAN) and US 4 137 180 (LEVER BROTHERS). Preferably the weight ratio of these additional softening materials to the total of the amine softening materials is less than 3:1, more preferred less than 1:1, especially preferred less than 0.5:1.

The composition can also contain one or more optional ingredients selected from non-aqueous solvents such as C_1-C_4 alkanols and polyhydric alcohols, rewetting agents, viscosity modifiers such as electrolytes or long (e.g. 25-40 EO) alkoxylated fatty alcohols, for example calcium chloride, antigelling agents, perfumes, perfume carriers, fluorescers, colourants, hydrotropes, antifoaming agents, antiredeposition agents, enzymes, optical brightening agents, opacifiers, stabilisers such as guar gum and polyethylene glycol, emulsifiers, anti-shrinking agents, anti-wrinkle agents, fabric crisping agents, anti-spotting agents, soil-release agents, germicides, linear or branched silicones, fungicides, anti-oxidants, anti-corrosion agents, preservatives such as Proxel, ascorbic acid, Bronopol (Trade Mark), a commercially available form of 2-bromo-2-nitropropane-1,3-diol, dyes, bleaches and bleach precursors, drape imparting agents, antistatic agents and ironing aids.

These optional ingredients, if added, preferably are present at levels up to 5% by weight of the composition.

The compositions according to the invention may be prepared by a variety of methods. One suitable method to prepare liquid products according to the invention is to form a molten mixture of the amine materials eventually in combination with other softening materials, and adding this premix to water under stirring to form a dispersion and thereafter adding the pH adjusting materials and any optional ingredients.

The invention will further be illustrated by means of the following examples.

EXAMPLE I

A di hardened tallow methyl amine (Armeen M2HT) was dispersed in water of ambient temperature to a concentration of 200 ppm of the amine. The pK_a of the amine is 4.5. For tests 1-6, 1 litre of the 200 ppm amine dispersion was adjusted to the pH as indicated with HCl. Pieces of terry towelling of a total weight of 40g were rinsed for 5 minutes in the amine dispersion. The pieces were line dried. The amount of deposited amine was determined by measuring the change in turbidity of the rinse liquor. A higher deposition percentage corresponds to a better softening.

The following results were obtained.

TEST	pH	% deposited amine
1	3.0 (pK_a-1.5)	95
2	3.5 (pK_a-1.0)	81
3	4.0 (pK_a-0.5)	68
4	4.5 (pK_a)	50
5	5.0 (pK_a+0.5)	40
6	6.0 (pK_a+1.5)	30

These results indicate that a good deposition (over 50%) can be obtained when the pH of the rinse liquor is equal to or below the pK_a of the amine. Especially good results are obtained when the rinse pH is at least 0.5 unit below the pK_a of the amine.

EXAMPLE II

The performance and stability of several amine containing liquid fabric softening compositions was tested as follows:

A wash load of 1.25 kg of terry towelling and 1.25 kg of cotton sheeting fabrics was washed at 40 ° C in a Miele 756 automatic with 100g of Persil Automatic (UK). 90 mls (corresponding to about 200 ppm for the amine concentration) of a rinse conditioner containing 5wt% Armeen M2HT, 1wt% tallow 35EO and a variable amount of pH adjusting material was added to the last rinse cycle. In table 3, the stability of the undiluted product, the pH of the undiluted product and the pH of the rinse water are given. A lower value for the pH of the rinse corresponds to a better softening performance.

TABLE 3

pH adjuster			undiluted product		rinse
type	pK_a	conc(M)	stability	pH	pH
HCl	<0.0	0.7	unstable	0.2	5.2
HCl	<0.0	0.9	unstable	0.1	4.4
HCl	<0.0	1.0	unstable	0.1	3.7
Oxalic	1.2	0.3	unstable	1.0	6.0
Oxalic	1.2	0.4	unstable	0.9	4.8
Oxalic	1.2	0.6	unstable	0.8	3.3
o-H_3PO_4	2.1	0.6	stable	1.3	5.6
o-H_3PO_4	2.1	0.9	stable	1.0	4.6
o-H_3PO_4	2.1	1.2	unstable	0.8	3.8
Malonic	2.8	0.5	stable	1.7	5.4
Malonic	2.8	0.7	stable	1.5	4.7
Malonic	2.8	0.9	stable	1.4	3.4
Tartaric	3.2	0.4	stable	1.8	5.7
Tartaric	3.2	0.5	stable	1.7	4.5
Tartaric	3.2	0.8	stable	1.5	3.9
Citric	3.1	0.3	stable	2.0	5.6
Citric	3.1	0.5	stable	1.8	4.5
Citric	3.1	0.9	stable	1.6	3.8
Succinic	4.2	1.0	stable	2.3	4.5
Succinic	4.2	1.5	stable	2.2	4.2

These results show that if acids of low pK_a such as HCl and Oxalic acid are used, then stable products which give the required pH in the rinse cannot be formulated. This illustrates the lower limit of 1.5 for the pK_a of the pH adjuster in liquid products. If orthophosphoric acid is used for pH adjustment, stable products may be formulated, but at higher levels of the acid instability occurs, with orthophosphoric acid, these high levels of acids ar however necessary to lower the pH of the rinse liquor to a value below the pK_a of the amine. Therefore for formulating Armeen M2HT systems, the use of orthophosphric acid as the pH adjusting material is less preferred.

If malonic, citric or tartaric acid are used stable compositions are obtained, which provide the preferred pH value in the rinse only at relatively low levels of the acid material. Similar results may be obtained by using lactic acid. These materials are therefore preferred for use in Armeen M2HT systems.

If succinic acid is used, also stable products are obtained, but high levels of the acid material are necessary to obtain the preferred pH in the rinse liquor, these high levels of acid materials are sometimes less preferred for cost reasons.

Claims

1. A fabric softening composition comprising one or more amine softening materials and one or more pH adjusting agents, wherein the pH of an aqueous liquor obtained by diluting said fabric softening composition to a concentration of 200 ppm of the amine materials has a pH which is equal to or below the pK_a of the amine materials.

2. A fabric softening composition according to claim 1, wherein the pH of the diluted amine liquor is at least 0.5 unit below the pK_a of the amine.

3. A fabric softener composition according to claim 1 or 2, wherein the amine is of the formula (I) as hereinbefore described.

4. A fabric softening composition according to one or more of the preceding claims, being a liquid comprising an aqueous base, wherein the pH adjusting agent satisfies the following equation:
$1.5 < pK_a$ (pH adjuster) $< pK_a$ (amine)

5. A fabric softening composition according to claim 4, wherein the pK_a of the pH adjuster is from 2.5 to 3.5.

6. A fabric softening composition according to claim 4 or 5, wherein the pH adjusting agents are selected

from the group or tartaric acid, lactic acid, citric acid and malonic acid or mixtures thereof.

7. A fabric softener composition according to claims 4 to 6, wherein the concentration of the pH adjusting material is from 0.25 to 1.0 mole per litre.

8. Use of one or more amine softening material and one or more pH adjusting agents in the manufacture of a fabric softening composition which when diluted to a concentration of 200 ppm of the amine material has a pH which is equal to or below the pK_a of the amine material for softening fabrics.