

"CONCENTRATED FABRIC SOFTENING COMPOSITION
AND METHODS FOR MAKING SAME"

The present invention relates to fabric softener compositions adapted for use in the rinse cycle of a laundering process and in particular to concentrated aqueous fabric softener compositions which are

5. stable at both low and high ambient temperatures, i.e. such compositions do not form a gel, and which are easily dispersed in water when used.

Compositions containing quaternary ammonium salts having at least one long chain hydrocarbyl group are commonly used to provide fabric softening benefits when employed in a laundry rinse operation; for example, see U.S. Patents 3,349,033; 3,644,203; 3,946,115; 3,997,453; 4,073,735 and 4,119,545.

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For most aqueous softener compositions

15. containing cationic quaternary ammonium compounds as active ingredients, the concentration of such cationic compounds has, in general, been limited to the range of about 3 to 6% by weight (see U.S. Patent 3,904,533 and U.S. Patent 3,920,565). Such a

20. low concentration is generally necessitated by the fact that such cationic compounds form gels in water systems at concentrations above about 8%, and while the use of electrolytes to lower the viscosity of such compositions is known (see in particular U.S. Patent 4,199,545), such electrolytes are far from

25. satisfactory. From a functional point of view, the electrolytes often do not perform as required particularly at concentrations of the cationic

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compounds in the neighbourhood of about 12-15%.

Further, while the performance of the electrolytes may alleviate some of the gelling problem, their use is far from satisfactory in providing a highly

5. concentrated aqueous system of cationic compounds which does not gel or severely change in viscosity within the usual range of temperatures encountered in the handling thereof, for example 0°F (about -18°C) up to about 140°F (about 60°C). In U.S.
10. Patent 3,681,241 a concentrated fabric softening emulsion is described which consists essentially of 3.5 to 6.5 parts by weight of a compound represented, for example, by distearyl dimethyl ammonium chloride, from 3.5 to 6.5 parts by weight of an
15. alkyl amido imidazolinium alkylsulphate, and from 0 to 3 parts by weight of a different but similar fatty amido imidazolinium alkylsulphate, the latter allegedly providing low temperature stability for the composition. The total content of active
20. ingredients contemplated ranges from about 8 to 13%.

In British Application 2053249A published 4th February, 1981, there are disclosed cationic fabric softening compositions containing 15 to 60% by weight of cationic softener, 25 to 75% by weight of

25. an aqueous medium, and 0.5 to 40% by weight of a specified water soluble polymer.

- In U.S. Patent 3,974,076 there are disclosed quaternary ammonium-containing softening compositions of conventional cationic concentrations, i.e. about
30. 3% to about 6%. These compositions are characterised

- by the very small particle size of the substantially water-insoluble quaternary ammonium softening compound, i.e. 90% by weight of the quaternary ammonium compounds exist as particles which will
5. pass through a 1.2 micron filter. The compositions are described as a combination of the cationic softener, a C₈ to C₂₀ alkyl alcohol with from about 0.1% to about 2.0% of a non-ionic surfactant having a HLB of from about 8 to about 15, and preferably
 10. from about 10 to about 14. The preferred non-ionics have a lipophilic hydrocarbyl moiety equivalent of 9 to 15 carbon atoms with 7 to 13 ethylene oxide hydrophilic moieties. This patent does not relate to the problem of stability of concentrated aqueous
 15. cationic softening compositions but rather to improving the level and uniformity of softening using conventional concentrations.

- Each of U.S. Patents 4,076,632; 4,157,307 and 4,233,164 discloses quaternary ammonium softening
20. compositions containing inter alia, "protonated" ethoxylated amine, but none of these disclose salts of the amine, let alone with high molecular weight organic acids (i.e. higher fatty acids e.g. C₁₂ to C₃₀; alkyl aryl sulphonic acids e.g. C₁₂ to C₁₈
 25. alkyl benzene sulphonic acids; C₁₂ to C₃₀ paraffin (alkyl) sulphonic acids; C₁₂ to C₃₀ olefin sulphonic acids; the mono- and di-phosphoric acid esters of C₈ to C₃₀ alcohols including the ethoxylates of such alcohols with from one to 100 moles of ethylene
 30. oxide). U.S. Patent 4,118,327 describes conventional

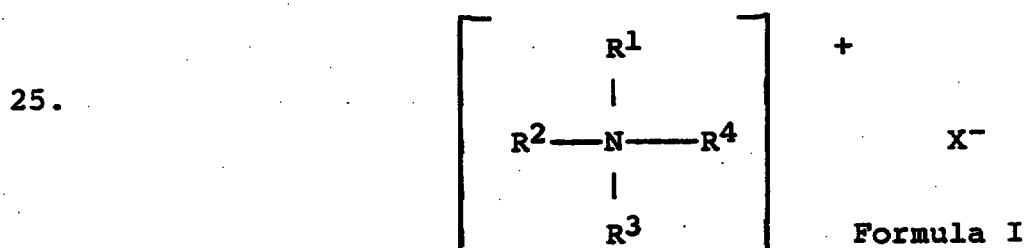
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cationic concentrations (0.1 to 10% preferably 1 to 8% by weight) with phosphate organoesters as anti-static agents.

5. The present invention provides low and high temperature stable, concentrated, aqueous softener compositions based upon quaternary ammonium softening compounds and a minor amount of an amine salt preferably of an ethoxylated long chain amine with a long chain organic acid and an additional
10. electrolyte. Water-soluble polymers such as polyethyleneglycol (e.g. M.W. 400) are a preferred optional ingredient.

15. The compositions of the present invention are stable aqueous compositions which contain a high concentration of the cationic fabric softener which is a water dispersible quaternary ammonium compound as hereinafter described, and an amine salt, also as hereinafter described.

20. According to the present invention a stable, aqueous, concentrated fabric softening composition comprises (A) 12-20% by weight of a cationic softener of the formula:



30. wherein the R^1 , R^2 , R^3 and R^4 each independently represent a C_1 to C_{30} hydrocarbyl group, preferably an alkyl or alkenyl

- group, or aryl group (e.g. a phenyl, tolyl or cumyl group); or an aralkyl group (e.g. a benzyl, or a phenethyl group); or a halo, amido, hydroxyl, or carboxy substituted version thereof; with the proviso that at least one of R^1 , R^2 , R^3 and R^4 representing a C_{14} to C_{30} and preferably C_{14} to C_{18} group, and the others are lower alkyl groups, and more preferably at least two R groups represent a C_{14} to C_{18} group and the others are lower alkyl groups of C_1 to C_4 (and most preferably methyl or ethyl), and X represents a water-solubilizing anion such as chloride, bromide, iodide, fluoride, sulphate methosulphate, nitrite, nitrate, phosphate or carboxylate (e.g. acetate, adipate, propionate, phthalate, benzoate or oleate); (B) 1 to 5.25% by weight of an amine salt and (C) 0.1 to 5% by weight of an additional electrolyte, the ratio of (A) to (B) being 40:1 to 2.6:1. The total softener concentration is preferably 12 to 15% by weight. Typical cationic compounds of formula I include the following:
- distearyl dimethyl ammonium chloride;
 - ditallow dimethyl ammonium chloride;
 - dihexadecyl dimethyl ammonium chloride;
 - distearyl dimethyl ammonium bromide;
 - di(hydrogenated tallow) dimethyl ammonium bromide;
 - distearyl, di(isopropyl) ammonium chloride;
 - distearyl dimethyl ammonium methosulphate.

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- The preferred amine salts contemplated herein are based upon ethoxylated long chain amines and long-chain organic acids. The amines are typically C₁₂ to C₃₀ aliphatic amines, and preferably C₁₂ to C₂₀ amines and admixtures thereof reacted with from one to about 100 moles of ethylene oxide. The amines may _____

- also be reacted with propylene or butylene oxide and then with ethylene oxide. The final oxyalkylated amine should be a water-soluble product. Of particular value are the amines derived from natural fatty acids such as those sold under the trade marks Armeen and Ethomeen and these generally comprise a mixed alkyl ranging from C₁₀ to C₁₈, or C₁₂ to C₁₆, or C₁₂ to C₁₅, or C₁₆ to C₁₈ and the like. Preferred ethoxylated amines are those containing from about 5 to about 50 moles of condensed ethylene oxides and more preferred are ethoxylated amines with about 10 to about 35 moles of condensed ethylene oxide. The most preferred compounds contain 12 to 20 moles of ethylene oxide.
5. The third ingredient is an electrolyte (ionic) material in an amount of from about 0.1 to about 5%, e.g. 0.5 to 1.5% by weight. The use of an electrolyte acts not only to control the viscosity but also assists in stabilizing the system against gelling and phase inversion at high temperatures, e.g. about 40°C. Particularly suitable electrolytes include sodium chloride and calcium chloride. Other useful electrolytes include sodium formate, sodium nitrite, sodium nitrate, sodium acetate, among others as well as water-soluble salts of other cations such as potassium, lithium, magnesium, ammonium and the like.
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Minor amounts of lower alkanols may be used particularly where it is desired to further modify the viscosity. In general, alcohols tend to lower the viscosity at ambient temperatures, although

- moderate amounts may effect a lowering of the phase inversion temperature. The preferred compositions of this invention exhibit phase inversion temperatures above about 80°C and preferably above about 90°C with amounts of alcohol in the range of about 1 to about 10% by weight. Particularly suitable alcohols are ethyl and isopropyl alcohol.
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- In addition to the foregoing components of the softening compositions of the present invention,
10. there may also be included numerous conventional, supplemental, and optional ingredients which do not adversely affect the stability and/or functional characteristics of the compositions of the present invention. Thus, for example, there may be present
15. the ubiquitous perfumes, dyes, pigments, opacifiers, germicides, optical brighteners, anti-corrosion agents (e.g. sodium silicate) water-soluble polymers, anti-static agents and the like. Where used, each may comprise from 0.01% to about 5% by weight of the
20. composition.

- It is, of course, recognized and understood that most available chemical materials and particularly those containing an hydrocarbyl moiety are generally mixtures of closely related moieties. Thus, the
25. long chain alkyl substituents (R) in the cationic compounds used in the present invention may be a single carbon length chain but are more preferably a mixture. In this regard a particularly useful quaternary set wherein the alkyl groups are derived
30. from tallow may contain about 35% C₁₆ and 60% C₁₈ and

minor amounts of C₁₄ and even others.

5. The fabric softening compositions of the present invention should have in addition to viscosity and phase stability, the requisite viscosity (i.e. for pourability) and water-dispersibility in the rinse cycle (or any other form of dilution prior to use) which the consumers have come to accept and demand from their use of the less concentrated products. Thus the products contemplated herein may have
10. viscosities ranging from about 30 cps to about 250 cps and preferably from about 40 cps to about 120 cps.

15. In addition to affording excellent dispersibility characteristics in water, the amine salts used herein contribute softening as well so that, for example, a concentration of 12% quaternary compound and 2% amine salt is not merely equivalent to twice a conventional 6% cationic composition but is almost 2 1/2 times as effective.

20. There are several general procedures for preparing compositions in accordance with the present invention, the final product varying somewhat in stability depending on which procedure is used. The procedure to be selected depends on
25. the components used and the procedures differ in the order of addition of the ingredients and the processing conditions.

30. According to a first aspect of the method a method of preparing the composition in accordance with the invention comprises first preparing an

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aqueous solution of the amine salt in warm water at a temperature up to about 80°C, thereafter adding the cationic softener in melted form to form a gel, cooling the said gel to below 40°C, and then adding electrolyte to break the gel. Preferably, the warm water temperature is about 70°C, the gel is cooled to just below 40°C and after the gel is broken the mixture is cooled to room temperature with stirring.

A typically preferred procedure (A) involves adding the nonionic material and colouring, if any, to the formula weight of water which is at about

- 70°C. To this solution there is slowly added the cationic softener in "melted" form (e.g. at 50-60°C) to which the amine salt has already been added. Usually a gel will form. The mixture is cooled to
5. about 40°C and then the electrolyte is added to break the gel. The composition is then cooled to room temperature with stirring. According to a second aspect of the method, a method of preparing the composition comprises first preparing an aqueous
10. solution of the amine salt in warm water at a temperature of up to about 80°C, adjusting the pH with alkaline material to above about 10, adding the cationic softener in melted form, readjusting the pH to below 7, cooling to about room temperature and
15. then adding electrolyte to adjust the viscosity.

- Procedure B is a modification of procedure (A) and involves adjusting the pH to about 12 before adding the melted cationic compound. In this case no gel forms. After cooling to about 40°C, the pH
20. is readjusted to 5 to 6, cooled with stirring to room temperature and then electrolyte is used to adjust the viscosity. According to a third aspect of the method, a method of preparing the composition comprises first preparing an aqueous solution of the
25. amine salt then adding electrolyte followed by the cationic softener in melted form and then cooling to room temperature. Still another procedure (C) involves adding the nonionic and electrolyte to at least 80% of the water which has been warmed (e.g.
30. to about 40°C), and then adding the cationic

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softener and amine salt as in procedure (A). Generally, no gel will form. The rest, if any, of the water is then added, and the composition is then cooled with agitation to room temperature.

5. The invention may be put into practice in various ways and a number of specific examples will be described to illustrate the invention with reference to the accompanying examples. Parts are by weight unless otherwise indicated.

10. EXAMPLE 1

Following Procedure (A) described above, 1 part of polyethylene glycol (MW.400) and 1.2 parts of 0.2% colour solution are dissolved in about 70 parts

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- of water at a temperature of about 70°C. To this solution are slowly added 17.6 parts of distearyl dimethyl ammonium chloride (75% active ingredient content and containing about 10% isopropanol and the balance water) in melted form (at 55°C) to which has been previously added 3.7 parts Ethomeen T25 and 1.3 parts of dodecyl benzene sulphonic acid with stirring. Ethomeen T25 is a tallow amine (40% C₁₆; 60% C₁₈) condensed with 15 moles of ethylene oxide.
5. A gel is formed. The gel is cooled down to about 40°C and then 0.5 parts of calcium chloride dihydrate (the electrolyte) are added. The mixture is cooled to room temperature (about 20°C) with stirring. A stable product results with a viscosity of about 100 cps.
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EXAMPLES 2a to 2d

The procedure of Example 1 is repeated utilizing the following parts of (A) cationic (active), (B) amine, (C) sulphonic acid and (D) electrolyte.

20. (a) A = 12; B = 1.0; C = 0.32; D = 0.5
 (b) A = 14; B = 1.5; C = 0.52; D = 0.5
 (c) A = 16; B = 1.8; C = 0.63; D = 0.7
 (d) A = 18; B = 2.5; C = 0.88; D = 1.0.

EXAMPLES 3a to 3c to 7a to 7e

25. Each of the five formulations listed in Examples 1 and 2 are repeated utilizing in place of distearyl dimethyl ammonium chloride the following:
 ditallow dimethyl ammonium chloride; (Example 3)
 distearyl dimethyl ammonium methosulphate;
 (Example 4)
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di(hydrogenated tallow) dimethyl ammonium
bromide; (Example 5)

di-hexadecyl dimethyl ammonium chloride;
(Example 6)

5. distearyl diethyl ammonium chloride; (Example 7).

EXAMPLE 8

- Examples 1 to 7 are repeated adding in all
instances 1 part of polyethylene glycol (MW400) with
the amine salt in the first step of the process of
10. the preparation.

- Polyethylene glycol (MW400) is illustrative of
low molecular weight, water-soluble polymers which
may be used if desired in the softening compositions
of the present invention. Among other useful
15. polymers reference is made to British published
application 2053249A described above which is hereby
incorporated herein by such reference thereto. The
compositions of the present invention may include
any and all of such polymers and other water-soluble
20. polymers as well. In the compositions of this
invention one may use from 0.1% to 20% by weight of
the total composition of these materials.

EXAMPLE 9

- Each of the foregoing Examples 1 to 8 is
25. repeated using as the electrolyte the following:
(a) sodium chloride
(b) sodium nitrate
(c) sodium formate
(d) ammonium bromide
30. (e) potassium chloride

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- (f) calcium nitrate
- (g) lithium acetate
- (h) magnesium chloride.

EXAMPLE 10

5. Each of Examples 1 to 9 is repeated, using the same ingredients but following Procedure (B) for making the compositions. In this procedure the change in the processing described in Example 1 involves adjusting the pH to 12 with sodium
10. hydroxide after dissolution of the amine salt (and polyethylene glycol where used), and readjusting the pH to 5-6 with hydrochloric acid after the addition of the cationic compound. At this point no gel forms as distinct from Procedure (A). The
15. electrolyte is added after the mixture has been cooled to room temperature.

EXAMPLE 11

- Each of Examples 1 to 9 is repeated again, using the same ingredients, but following Procedure (C) to
20. prepare the compositions.
- In this procedure the amine salt (and the water soluble polyethylene glycol where used) is dissolved in 80% of the formula weight of water at a temperature of 35-40°C. The electrolyte is then
25. added, followed by the melted cationic compound. The remaining formula weight of water is then added and thereafter the mixture is cooled to room temperature with stirring.

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- The aqueous softening compositions of the present invention are generally applicable as other such compositions, and are particularly useful in the rinse cycle of an automatic laundry machine. In
5. such operations as well as in any other desired method of treating clothes, the compositions are usually employed to provide generally an active concentration of from about 0.005% to 0.3% based on the weight of clothes treated preferably 0.07% to
10. about 0.2% and most preferable from about 0.01% to about 0.15%.

- The polymers described in G.B. 2053249A referred to above should be water-soluble under user's conditions, and a 20% aqueous solution of the
15. polymer should have a viscosity (η) of ≤ 50 , preferably ≤ 30 and especially preferably ≤ 15 cP, as measured at 25°C and 110sec.⁻¹ in a Haake Viscometer. Said 20% aqueous solution should also show a vapour pressure equal to or lower than the
20. vapour pressure of a 2% aqueous solution of polyethylene glycol with a molecular weight of 6,000, preferably equal to or lower than that of a 10% aqueous solution of said polyethyleneglycol, and particularly preferably equal to or lower than that
25. of an 18% aqueous solution of said polyethylene-glycol. The said aqueous polymer solution can be of water and polymer only, or can include solvent-containing media normally derived from the raw materials or additives, or include additives
30. specifically designed to improve the vapour pressure

lowering capacity of the polymer, or, in the case of ionic polymers, include adjustments to pH in order to optimise ionisation. Such vapour pressure measurements can be obtained using a Hewlett Packard

5. (Registered Trade Mark) vapour pressure osometer, using an operating temperature of 34.5°C or using any other suitable vapour measuring device.

10. The polymer should furthermore have a molecular weight of at least 400, preferably at least 4,000 and particularly preferably at least 6,000.

It is desirable, furthermore, that the polymer does not negatively interact with any of the other ingredients of the composition.

15. Suitable examples of the polymer can be thus obtained from the polyalkyleneglycols, the polyalkylene imines, dextran and other natural or synthetic (co)polymers, as long as they meet the above criteria.

20. Mixtures of two or more polymers of the same type or of different type may also be used.

25. A preferred class of polymers comprises polyethyleneglycols with an average molecular weight of about 1,000 to about 6,000. These polymers, and especially those with an average molecular weight of 4,000 or 6,000, are particularly suitable for compositions of the invention with a high level of relatively water-insoluble cationic fabric-softening agent.

30. Other typical examples of suitable polymers are dextran with a molecular weight of 10,000 and polyethylene imine with a molecular weight of 45-750.

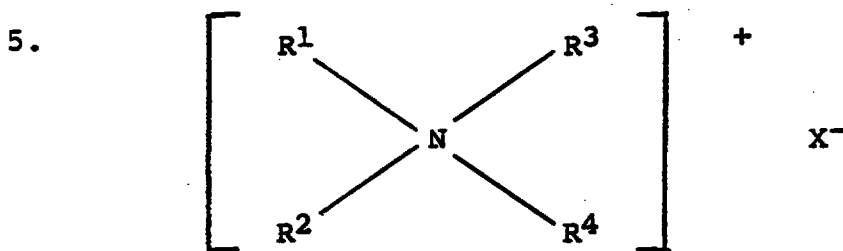


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CLAIMS

1. A stable, aqueous, concentrated fabric softening composition comprising (A) 12 to 20% by weight of a cationic softener of the formula:



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wherein R^1 , R^2 , R^3 and R^4 each independently represent a C_1 to C_{30} hydrocarbyl radical with at least one of R^1 , R^2 , R^3 and R^4 representing a C_{14} to C_{30} group and the others are C_1 to C_4 alkyl groups and X represents a water solubilizing anion; (B) 1 to 5.25% by weight of an amine salt and (C) 0.1 to 5% by weight of an additional electrolyte, the ratio of (A):(B) being in the range 40:1 to 2.6:1.

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2. A composition as claimed in Claim 1 in which (A) is distearyl dimethyl ammonium chloride.

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3. A composition as claimed in Claim 1 or Claim 2 in which the amine salt is the reaction product of a nonionic ethoxylated amine containing an average of about 15 moles of ethylene oxide and an acid.

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4. A composition as claimed in Claim 1, 2 or 3 in which the amount of compound (A) is about 12% and that of compound (B) is about 2%.
5. 5. A composition as claimed in any one of Claims 1 to 4 in which the total softener concentration is 12 to 15% by weight.
10. 6. A stable aqueous concentrated fabric softening composition as claimed in Claim 1 substantially as specifically described herein with reference to the examples.
15. 7. A method for preparing a composition as claimed in any one of Claims 1 to 6 which comprises first preparing an aqueous solution of the amine salt in warm water at a temperature up to about 80°C, thereafter adding the cationic softener in melted form to form a gel, cooling the said gel to
20. below 40°C, and then adding electrolyte to break the gel.
25. 8. A method as claimed in Claim 7 in which the warm water temperature is about 70°C, the gel is cooled to just below 40°C and after the gel is broken the mixture is cooled to room temperature with stirring.
30. 9. A method for preparing a composition as claimed in any one of Claims 1 to 6 which comprises



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- first preparing an aqueous solution of the amine salt in warm water at a temperature of up to about 80°C, adjusting the pH with alkaline material to above about 10, adding the cationic softener in
5. melted form, readjusting the pH to below 7, cooling to about room temperature and then adding electrolyte to adjust the viscosity.

10. A method for preparing a composition as
10. claimed in any one of Claims 1 to 6 which comprises first preparing an aqueous solution of the amine salt then adding electrolyte followed by the cationic softener in melted form and then cooling to room temperature.

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