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B-1853 Strombeek-Bever (BE)(54) **Use of alkaline polyammonium salts to increase cationic density in fabric softeners.**(57) The invention relates to the use of a composition comprising cationic fabric softeners, preferably quaternary ammonium esters and (C₃-C₁₀) alkyl/aryl polyammonium salts.

These polyammonium salts are used to replace partially or fully calcium chloride to aid the cationic fabric softeners in depositing on fabrics while reducing the inter-cationic interferences usually leading to low deposition densities.

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Field of the Invention

The invention relates to the use of a composition comprising cationic fabric softeners, preferably quaternary ammonium esters and (C₃-C₁₀) alkyl/aryl polyammonium salts.

These polyammonium salts are used to replace partially or fully calcium chloride to aid the cationic fabric softeners in depositing on fabrics while reducing the inter-cationic interferences usually leading to low deposition densities.

Background of the Invention

Compositions containing polyammonium salts and conventional fabric softeners are disclosed in US application 07/88/979. However, no mention of the use of these polyammonium salts as deposition density aid is disclosed in this document. FR-A-1581392 discloses diamine salts falling within the definition of the polyammonium salts of the present invention. However, these diamine salts are disclosed in the context of washing powders including anionic detergents.

GB-A-2006237 discloses polymers comprising a monomere of alky-diamines. These monomeres also fall within the definition of the polyammonium salts of the present invention. The compositions disclosed are used in hair care formulations and the polymers derived from the polyammonium monomeres are said to have improved compatibility with anionic surfactants.

EP-A-69948 and JP-A-90012203 disclose polyammonium compounds in the context of fabric treatment compositions. However, no indication of these compounds falling within the definition of the present invention has been found. The problem underlying the present invention is to provide viscosity control and stability of fabric softening compositions, to increase the density of cations which can be deposited on a fabric fiber and, at the same time, to perform anionic scavenging for carry-over detergent from the main wash. These problems had all been solved individually before, however, their combination with the additional condition that no adverse effects in other characteristics of a fabric softener composition would be acceptable is the main objective of the present invention.

Summary of the Invention

It now has been found surprisingly that the use of soluble carbohydrate polyammonium salts replacing calcium chloride does satisfy the complex objective of the present invention. Therefore, the present invention relates to the use of soluble polyammonium salts for viscosity control, deposition density aid and anionic scavenging in rinse added fabric softening compositions.

The fabric softening compositions comprise insoluble fabric softening agent and, at least 0.1 % by weight of a (C₃-C₁₀)alkyl or aryl polyammonium salt. Preferred embodiments according to the present invention are indicated in the dependent claims attached to this specification.

In an alternative aspect to the polyammonium salts partially quaternized or non-quaternized polyammonia can be used provided the rinse added composition is used in an environment such that the non-quaternized or partially non-quaternized ammonia becomes protonated through acidic buffering of the rinse liquid. Any useful acids buffering the rinse liquid can be used in this context and the ammonia can be seen as the precursor of quaternized ammoniums.

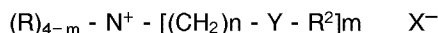
Detailed description of the Invention

In the following the essential compounds and optional compounds of the composition as used in the invention will be described separately. Percentages, when they are indicated, are by weight of the final composition. For optional compounds, reference is made here to the general knowledge of those skilled in the art and the prior art documents mentioned herein.

The cationic fabric softening compound.

The essential fabric softening compound of the present invention is typically a non-soluble quaternized ammonium, preferably a di-ester quaternary ammonium. Preferably the cationic fabric softening compound is present in a total amount of at least 15 %, more preferably in an amount of 15 % to 25 %, not accounting for optional cationic fabric softeners.

According to the present invention the preferred ester ammonium can have the general formula :



wherein

each Y = -O-(O)C-, or -C(O)-O-;

5 m = 1, 2 or 3, preferably 2;

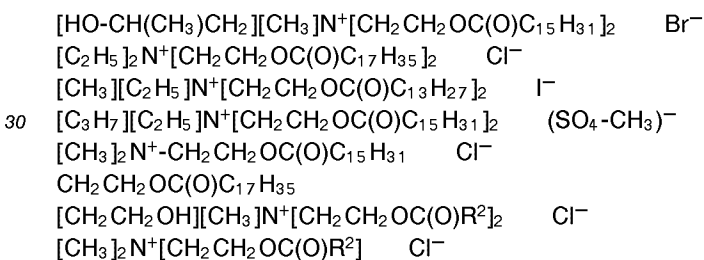
each n = 1 to 4

each R substituent is a short chain C₁-C₆, preferably C₁-C₃ alkyl or hydroxyalkyl group, e.g., methyl (most preferred), ethyl, propyl, hydroxyethyl, and the like, benzyl or mixtures thereof; each R² is a long chain C₁₂-C₂₂ hydrocarbyl, or substituted hydrocarbyl substituent, preferably C₁₅-C₁₉ alkyl and/or alkylene, most preferably C₁₅-C₁₇ straight chain alkyl and/or alkylene; and the counterion, X⁻, can be any softener-compatible anion, for example, chloride, bromide, methylsulfate, formate, sulfate, nitrate, and the like.

It will be understood that substituents R and R² can optionally be substituted with various groups such as alkoxy or hydroxyl groups, and/or can be saturated, unsaturated, straight and/or branched so long as the R² groups maintain their basically lipophilic character. The preferred compounds can be considered to be di-ester variations of ditallow dimethyl ammonium chloride (DTDMAC), which is a widely used fabric softener. At least 80% is in the di-ester form, and from 0 % to about 20% can be monoester.

As used herein when the di-ester is specified, it will include the monoester that is normally present, but not additional monoester that is added. For softening, the percentage of di-ester should be as high as possible, preferably more than 90%.

20 The above compounds used as the primary active softener ingredient in the practice of this invention can be prepared using standard reaction chemistry. In one synthesis of a di-ester variation of DTDMAC, an amine of the formula RN(CH₂CH₂OH)₂ is esterified at both hydroxyl groups with an acid chloride of the formula R²C(O)C₁, then quaternized with an alkyl halide, RX₂, to yield the desired reaction product (wherein R and R² are as defined hereinbefore). The following are non-limiting examples (wherein all long-chain alkyl substituents are straight-chain):



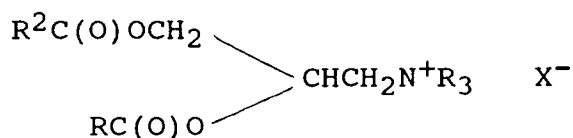
35 where -C(O)R² is derived from soft or hard tallow, or mixtures thereof.

Since the foregoing compounds (di-esters) are somewhat labile to hydrolysis (hence their beneficial degradability), they should be handled rather carefully when used to formulate the compositions herein. For example, stable liquid compositions herein are formulated at a pH in the range of about 2 to about 5, preferably from about 2 to about 4.5, more preferably from about 2 to about 4. The pH can be adjusted by the addition of a Bronsted acid. pH ranges for making stable softener compositions containing di-ester quaternary ammonium fabric softening compounds are disclosed in U.S. 4,767,547.

Examples of suitable Bronsted acids include the inorganic mineral acids, carboxylic acids, in particular the low molecular weight (C₁-C₅) carboxylic acids, and alkylsulfonic acids. Suitable inorganic acids include HCl, H₂SO₄, HNO₃ and H₃PO₄. Suitable organic acids include formic, acetic, methylsulfonic and ethylsulfonic acid. Preferred acids are hydrochloric and phosphoric acids. The presence of the aromatic acids which are useful in the present invention also helps to stabilize the di-ester compounds.

The preferred di-ester quaternary ammonium fabric softening compound (DEQA) can also have the general formula :

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wherein each R, R² and X have the same meanings as before. Such compounds include those having the formula :



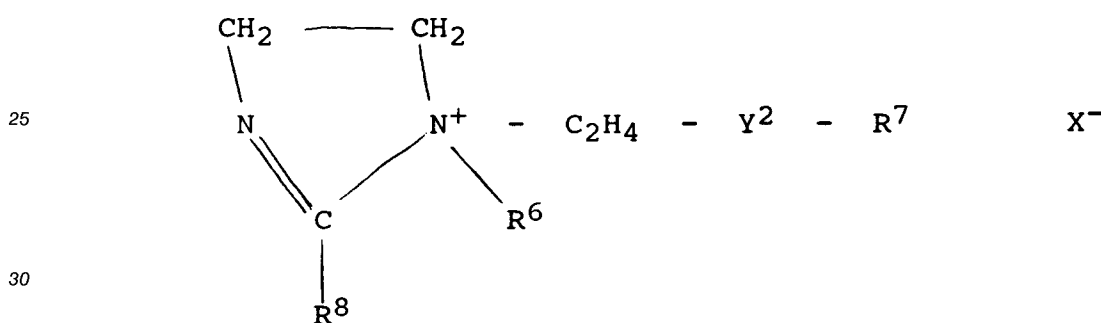
where $-\text{OC}(\text{O})\text{R}^2$ is derived from soft or hard tallow, or mixtures thereof.

5 Preferably each R is a methyl or ethyl group and preferably each R^2 is in the range of C_{15} to C_{19} . Degrees of branching, substitution and/or non-saturation can be present in the alkyl chains. The anion X^- in the molecule is preferably the anion of a strong acid and can be, for example, chloride, bromide, iodide, sulfate and methyl sulfate; the anion can carry a double charge in which case X^- represents half a group. These compounds, in general, are more difficult to formulate as stable liquid compositions. These types of
10 compounds and general methods of making them are disclosed in U.S. 4,137,180.

For stability of the composition and to enhance concentratability, as well as the derived isotopic characteristic, it is beneficial to have a high level of unsaturation in the lipophilic long chain hydrocarbons. An iodine value of above 30 up to 100, preferably above 50, has been found to be beneficial. Also beneficial, particularly if the iodine value is not above 70, are double bonds of the cis configuration due to
15 their melting point difference vs trans double bonds.

Other cationic materials with ring structures such as alkyl imidazoline, imidazolinium, pyridine, and pyridinium salts having a single C_{12} - C_{30} alkyl chain can also be used. Very low pH is required to stabilize, e.g. imidazoline ring structures. Some alkyl imidazolinium salts useful in the present invention have the general formula :

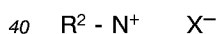
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wherein Y^2 is $-\text{C}(\text{O})-\text{O}-$, $-\text{O}-(\text{O})-\text{C}-$, $-\text{C}(\text{O})-\text{N}(\text{R}^5)-$, or $-\text{N}(\text{R}^5)-\text{C}(\text{O})-$

35 in which R^5 is hydrogen or a C_1 - C_4 alkyl radical; R^6 is a C_1 - C_4 alkyl radical; R^7 and R^8 are each independently selected from R and R^2 as defined hereinbefore for the single-chain cationic surfactant with only one being R^2 .

Some alkyl pyridinium salts useful in the present invention have the general formula :



wherein R^2 and X^- are as defined above. A typical material of this type is cetyl pyridinium chloride.

Further optional cationic and other softening compounds have been described or referred to in PCT application US-93-04107 filed May 3, 1993.

45 The fabric softener compositions optionally further contain quaternary - di or poly - ammoniums as described in detail in EP-A-503155 and EP-A-507003. These ammoniums are non-soluble cationic fabric softeners.

Polyammonium Salt

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(C_3 - C_{10}) alkyl or aryl polyammonium salts, or the ammonia precursors in a protonating environment are used according to the present invention for viscosity control, as deposition density aid and for anionic scavenging in rinse added fabric softening compositions. They are present in the fabric softening compositions in amounts of at least 0.1 %, preferably from 0.1 % to 5 %, most preferably from 0.2 % to 1
55 % by weight of the composition.

Hereinafter the polyammonium salts will be described with the nitrogen in its ammonium state but, as indicated above, they can be used with one or all nitrogens in their ammonia state, provided that they become protonated upon use. This is ensured by having sufficient protons available e.g. by the presence of

an acid as described above.

Preferred polyammonium salts are (C₃-C₈) alkyl polyammonium salts, particularly di-ammonium salt. Examples of such salts are

- 1,5-di-ammonium-2-methyl-panthene di-chloride.
- 5 - 1-ammonium-chloride-5-ammonia-hexoic acid (lysine-monohydrochloride).

While not wishing to be bound by theory, it has been considered by the inventors that these compounds have a substantially better viscosity control, deposition density aid and anionic scavenging because they distance the positive charges, while keeping them connected within one molecule.

This "partial individualisation of charges" can be compared for di-ammoniums with a model of two positive charges connected by a string which provides a high level of independence between the charges in comparison to a double charged calcium. On the other hand the density of the two charges connected by the string is higher than two independently charged molecules, since the string length is small relative to the distance which would be reached by electrical repellence for an even distribution of independently charged molecules on an identical number of charges.

15 Using the polyammonium salts provides a better control of the viscosity of the composition in that the polyammonium salts allow lower and higher temperatures without unacceptable viscosity conditions (i.e. gelling at low temperatures, watery appearance at high temperatures) relative to a comparably formulated composition using CaCl₂.

Further the use of the polyammonium salts allows better scavenging of carry over anionic surfactants (which is possibly due to the "partial individualisation of charges") and hence prevents depletion of the active cationic softening compound.

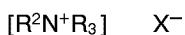
Further the limited string length between the "partially individualized charges" helps to bridge electrical repellent surface forces between deposited fabric softener actives and thereby aids in the deposition density of rinse added fabric softeners.

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Optional ingredients

As an optional viscosity modifier single long chain cationic surfactants, which are water soluble, can be present in amounts of 0% up to 15%. Such single long-chain-alkyl surfactants useful in the present invention are, preferably quaternary ammonium salts of the general formula:

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wherein the R² group is C₁₀-C₂₂ hydrocarbon group, preferably C₁₂-C₁₈ alkyl group or the corresponding ester linkage interrupted group with a short alkylene (C₁-C₄) group between the ester linkage and the N, and having a similar hydrocarbon group, e.g. a fatty acid ester of choline, preferably C₁₂-C₁₄ (coco) choline ester and/or C₁₆-C₁₈ tallow choline ester. Each R is a C₁-C₄ alkyl or substituted (e.g. hydroxy) alkyl, or hydrogen, preferably methyl, and the counterion X⁻ is a softener compatible anion, for example, chloride, bromide, methyl sulfate, etc.

40 The ranges above represent the amount of the water soluble single-long-chain-alkyl cationic surfactant which is added to the composition of the present invention. The ranges do not include the amount of monoester which is already present in the essential fabric softening compound.

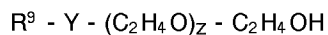
The long chain group R², of the single-long-chain-alkyl cationic surfactant, typically contains an alkylene group having from about 10 to about 22 carbon atoms, preferably from about 12 to about 18 carbon atoms. This R² group can be attached to the cationic nitrogen atom through a group containing one, or more, ester, amide, ether, amine, etc., preferably ester, linking groups which can be desirable for increased hydrophilicity, biodegradability, etc. Such linking groups are preferably within about three carbon atoms of the nitrogen atom. Suitable biodegradable single-long-chain alkyl cationic surfactants containing an ester linkage between the nitrogen and the long chain are described in U.S. 4,840,738.

50 It will be understood that the main function of the water-soluble cationic surfactant is to lower the viscosity and/or increase the dispersibility of the essential fabric softener compound and it is not therefore, essential that the cationic surfactant itself have substantial softening properties, although this may be the case. Also, surfactants having only a single long alkyl chain, presumably because they have greater solubility in water, can protect the essential fabric softener compound from interacting with anionic surfactants and/or detergent builders that are carried over into the rinse.

55 Another optional compound improving the viscosity of highly concentrated fabric softening compositions are non-ionic surfactants. Suitable non-ionic surfactants to serve as viscosity/dispersibility modifier include addition products of ethylene oxide and, optionally, propylene oxide, with fatty alcohols, fatty acids, fatty

amines, etc.

Any of the alkoxyated materials of the particular type described hereinafter can be used as the non-ionic surfactant. The non-ionics are used at a level of from 0% to about 15%. Suitable compounds are substantially water-soluble surfactants of the general formula :



wherein R^9 is selected from the group consisting of primary, secondary and branched chain alkyl and/or acyl hydrocarbyl groups; primary, secondary and branched chain alkenyl hydrocarbyl groups; and primary, secondary and branched chain alkyl- and alkenyl-substituted phenolic hydrocarbyl groups; said hydrocarbyl groups having a hydrocarbyl chain length of from 8 to about 20, preferably from about 10 to about 18 carbon atoms. More preferably the hydrocarbyl chain length is from 16 to 18 carbon atoms. In the general formula for the ethoxylated non-ionic surfactants herein, Y is typically -O-, -C(O)O-, -C(O)N(R)-, or -C(O)N- $(R^9)R$ -, in which R^9 , and R, when present, have the meanings given hereinbefore, and/or R can be hydrogen, and z is at least about 8, preferably at least about 10-11. Performance and, usually, stability of the softener composition decrease when fewer ethoxylate groups are present.

Examples of non-ionic surfactants are disclosed in further detail in PCT application US-93-04107 filed May 3, 1993. All of the typical fabric softener compounds usual in the art may further be present in the compositions according to the present invention, in particular enzymes (protease, lipase, cellulase and amylase, especially cellulase), perfumes, dyes, solvents, polymers, bacterial and fungal stabilizers and other compounds.

Claims

1. Use of a polyammonium salt for viscosity control, as deposition density aid and for anionic scavenging in rinse added fabric softening compositions, said fabric softening compositions comprising
 - a) a cationic fabric softening agent and
 - b) at least 0.1 % by weight of a (C_3-C_{10}) alkyl or aryl polyammonium salt.
2. Use according to claim 1 characterized in that the cationic fabric softening agent comprises a quaternized ester ammonium, preferably a quaternized di-ester ammonium.
3. Use according to any of the previous claims characterized in that said cationic fabric softening agent is present at an amount of at least 15 % by weight, preferably 15 % to 25 % by weight.
4. Use according to any of the previous claims characterized in that the polyammonium salt is a (C_3-C_8) alkyl polyammonium salt.
5. Use according to any of the previous claims characterized in that the polyammonium salt is a di-ammonium salt.
6. Use according to any of the previous claims characterized in that the polyammonium salt is present in an amount from 0.1 % to 5 %, preferably from 0.2 % to 1 %, by weight.
7. Use according to any of the previous claims characterized in that the polyammonium salt is present as partially quaternized or non-quaternized ammonia and only becomes protonated during the use in the rinse.



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EUROPEAN SEARCH REPORT

Application Number
EP 93 20 2884

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	WO-A-93 16157 (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN) * page 9, formula V * * claims * ---	1-6	C11D3/00 C11D1/645 C11D3/30
X	EP-A-0 165 138 (STEPAN EUROPE) * page 2, line 14 - page 5, line 3 * * page 7, line 14 - page 8, line 35; claims * ---	1-6	
X	EP-A-0 296 995 (COTELLE S.A.) * page 3, line 44 - page 5, line 15 * * page 5, line 57 - page 6, line 25 * * page 6, line 44 - line 47; claims * ---	1-6	
X	DATABASE WPI Week 8346, Derwent Publications Ltd., London, GB; AN 83-818125 & JP-A-58 172 308 (AJINOMOTO KK) 11 October 1983 * abstract * ---	1-7	
D	& JP-B-2 012 203 (AJINOMOTO KK) ---		TECHNICAL FIELDS SEARCHED (Int.Cl.6)
D,A	EP-A-0 507 003 (REWO CHEMISCHE WERKE GMBH.) * the whole document * ---	1	C11D
D,A	EP-A-0 069 948 (HOECHST AG.) * the whole document * ---	1	
A	EP-A-0 060 003 (THE PROCTER & GAMBLE COMPANY) * claims * -----	1-7	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 8 March 1994	Examiner Blas, V
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	