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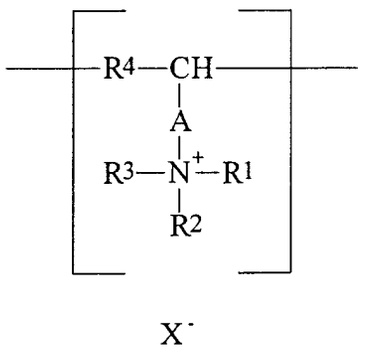
(54) Use of polymers in laundry cleaning

(57) A detergency enhancing polymer is used in a laundry cleaning operation to improve removal of oily and/or greasy soil from cotton fabrics. This polymer is a homopolymer or copolymer containing one or more monomer units independently selected from those of formula (I)



(I)

wherein -A- is selected from groups of formula $-R^5-$, $-R^5-(CO)-R^6-$, $-R^5-(CO)-O-R^6$, $-R^5-O-(CO)-R^6-$, $-R^5-(CO)-NH-R^6-$, $-R^5-NH-(CO)-R^6-$, wherein R^5 and R^6 are independently absent, or represent C_{1-3} alkyl groups;

R^1, R^2 and R^3 are independently selected from hydrogen, C_{1-3} alkyl, C_{1-3} alkenyl, hydroxy-C_{1-3} alkyl and C_{5-8} cycloalkyl groups; and

R^4 is selected from groups as defined for A above;

wherein R^3 may also represent a bridge, group with the group R^4, said bridging group being selected from groups as defined for A above; and

X - is a monovalent anion or an n'th part of an n-valent anion.

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Description

Field of the Invention

[0001] The present invention relates to a novel use of certain classses of polymer in the cleaning of laundry fabrics.

Background of the Invention

[0002] Compositions for the washing of laundry items traditionally contain one or more surfactants as well as other components. The most common class of surfactant in such compositions comprises the anionic surfactants, especially synthetic non-soap anionics Often, one or more such anionic surfactants are used together in a blend with one or more nonionic surfactants. Further, although anionic and cationic surfactants are often incompatible, due to the their tendency to form a complex, recently, there have been several proposals to utilise certain compatible anionic and cationic surfactant combinations in laundry wash products.

[0003] Nevertheless, there is still a need to find surfactant systems which give better removal of oily/greasy soil from cotton fabrics. The present invention solves this problem by use of certain cationic polymers (as defined hereinbelow) in products and processes for the cleaning of laundry items. One preferred such polymer is a dimethyldiallyl ammonium chloride polymer (poly-DMDAAC). Previously, cationic polymers in general have been used in a wide range of household cleaning and personal wash applications.

[0004] For example, cationic polymers have been widely used in dishwasher rinse aid products. For example, it is known from EP-A-0 167 382, EP-A-0 342 997 and DE-A-26 16 404 to mix cationic polymers with surfactant in such product, in order to obtain clean surfaces as free from streaks as possible.

[0005] EP-A-0 167 382 describes liquid detergent compositions which can contain cationic polymers as thickeners. Hydroxypropyltrimethyl ammonium guar, copolymers of aminoethylmethacrylate and acrylamide, and copolymers of DMDAAC and acrylamide are described as particularly suitable cationic polymers.

[0006] DE-A-26 16 404 describes cleaning preparations for glass and, containing cationic cellulose derivatives. These materials are said to give better drainage of water, to produce clean, streak-free glass.

[0007] WO-A-97/09408 discloses use of cationic polymers selected from cationic polymers of copolymers of monomers such as trialkyl ammonium alkyl(meth)acrylate or - acrylamide, DMDAAC and with other counter-ions; polymer-like reaction products of ethers or esters of polysaccharides with ammonium side groups, in particular guar, cellulose and starch derivatives; polyadducts of ethylene oxide with ammonium groups; quaternary ethylene imine polymers and polyesters and polyamides with quaternary side groups as soil-release compounds in dishwasher rinse aids.

[0008] Cationic polymers are also usable in hard surface cleaners. For example, EP-A-0 467 472 describes e.g. cleaning preparations for hard surfaces, containing cationic homopolymers and/or copolymers as soil-release polymers. These polymers comprise quaternised ammonium alkyl-methacrylate groups as monomer units. These compounds are used in order to render the surfaces such that the soil can be removed more easily during the next cleaning process.

[0009] EP-A-0 342 997 describes all-purpose cleaners which can contain cationic polymers, wherein in particular polymers with imino groups are used.

[0010] Another known use of such polymers is in hair shampoos. WO 97/42281 discloses compositions containing sugar-based nonionic surfactants and copolymers of acrylamide and DMDAAC to improve the tactile properties of such surfactants. Use in dishwashing applications is also mentioned.

[0011] In laundry washing/rinsing applications, several uses for cationic polymers have been proposed. Thus, JP-A-04 153300 discloses use of poly-DMDAAC in compositions containing cationic/amphoteric surfactants to enhance softness in the washing of delicate items.

[0012] Use of poly-DMDAAC as a greying-inhibitor in nonionic surfactant based compositions for washing laundry items is disclosed in DD-A-296 307.

[0013] JP-A-62 018500 discloses laundry detergent creams based on soap blends and cationic polymers such as poly-DMDAAC.

[0014] There is also a very large number of prior disclosures of cationic polymers used as dye fixers in laundry cleaning products, i.e. as materials for reducing the amount of dye released from fabrics, have been described in a number of references. For example, EP-A-0 462 806 describes use of such materials in rinse phase products to give protection against dye transfer during subsequent washes.

[0015] JP-A-07 316590 discloses detergent compositions containing cationic polymers, including poly-DMDAAC for anti-dye transfer and/or anti-soil redeposition aids. These compositions are typically bends of anionic and nonionic surfactants. However, there is no disclosure of using such a polymer to assist removal of oily/greasy stains.

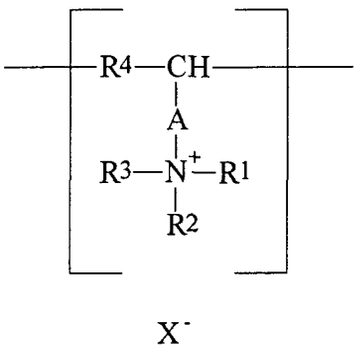
[0016] GB-A-2 323 385 discloses detergent compositions with a cationic dye-fixing ingredient. A small number of examples contains poly-DMDAAC with a molecular weight in the range 2,000 to 20,000, as a cationic dye fixing agent.

[0017] The structure and composition of aqueous mixture of sodium dodecyl sulphate, hexaethylene glycol monododecyl ether and poly-DMDAAC at the air-water interface, has been described in a number of references, namely J. Penfold et al, Langmuir **1995**, *11*, 2496-2503, J. Penfold et al, Colloids and Surfaces A, **1997**, *128*, 107-117, A. Creeth et al, J. Chem. Soc., Faraday Trans., **92,** *4*, 589-594, and L. Yingjie et al, Langmuir **1995,** *11*, 2486-2492. A wide range of model compositions to explore these phenomena are disclosed in these references.

[0018] The present inventors have now found that certain polymers containing DMDAAC and its analogues can be used in laundry cleaning products, e.g. in products for washing or rinsing.

Definition of the Invention

[0019] Thus, a first aspect of the invention now provides use of a detergency enhancing polymer in a laundry cleaning operation to improve removal of oily and/or greasy soil from cotton fabrics, said detergency enhancing polymer being a homopolymer or copolymer containing one or more monomer units independently selected from those of formula (I)



(I)

wherein

-A- is selected from groups of formula -R^5-, -R^5-(CO)-R^6-, -R^5-(CO)-O-R^6, -R^5-O-(CO)-R^6-, -R^5-(CO)-NH-R^6-, -R^5-NH-(CO)-R^6-, wherein R^5 and R^6 are independently absent, or represent C_{1-3} alkyl groups;

R^1, R^2 and R^3 are independently selected from hydrogen, C_{1-3} alkyl, C_{1-3} alkenyl, hydroxy-C_{1-3} alkyl and C_{5-8} cycloalkyl groups; and

R^4 is selected from groups as defined for A above;

wherein R^3 may also represent a bridging group to the group R^4, said bridging group being selected from groups as defined for A above; and

X - is a monovalent anion or an n'th part of an n-valent anion.

[0020] The invention also includes use of the detergency enhancing polymer as an oily and/or greasy soil improvement agent in the manufacture of a laundry cleaning product.

[0021] Any reference herein to an alkyl group includes reference to both straight and branched forms unless explicitly stated to the contrary.

Detailed Description of the Invention

[0022] The present invention typically provides use of the detergency enhancing polymer to assist removal of oily and/or greasy soil from fabrics during a laundry cleaning operation, for example by delivering said polymer in a laundry washing composition or in a laundry rinse composition, for example a fabric softening composition. The fabrics are then contacted by a wash or rinse liquor, as appropriate, in which the composition is dissolved or dispersed.

[0023] Without being bound by any particular theory or explanation, it is believed that when anionic surfactant is present, the detergency enhancing polymer mitigates against the formation of liquid crystalline phases at the soil/wash liquor interface. Moreover, only relatively small amounts of total anionic surfactant-polymer complex are needed to exert the effect, leaving the remainder of the anionic free to assist other cleaning functions in the wash liquor. On the

other hand, when no anionic surfactant is present (e.g when the detergency enhancing polymer is provided in a rinse cycle product such as a fabric conditioner, for example comprising cationic and/or nonionic surfactant), some of the detergency enhancing polymer remains on the fabric to provide the aforementioned effect when the fabric is next washed using a main wash composition containing anionic surfactant.

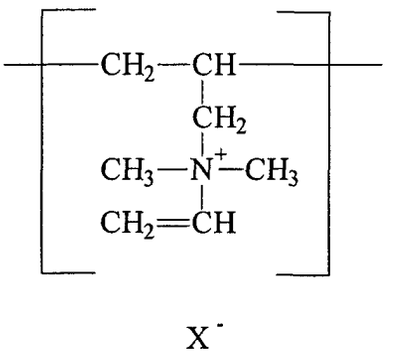
The Polymer

[0024] The detergency enhancing polymer can be a homopolymer or copolymer. Random, block and mixed block/random copolymers are all possible. The polymer may comprise one or more polymers which include one or more monomer units of formula (I).

[0025] Preferably, the monomer units of formula (I) are those where A is methylene ($-CH_2-$) or carbonyl (-CO-) and R^4 is methylene ($-CH_2-$) or ethylene ($-CH_2CH_2-$).

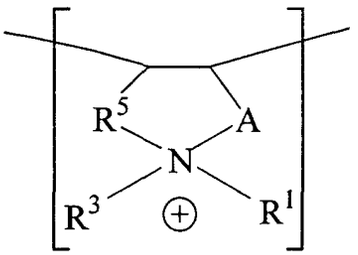
[0026] Especially preferred are polymers containing at least some monomer units of formula (I) in which A is methylene, R^1 and R^2 are methyl, and R^3 and R^4 together represent
-(CH-)-CH_2-, i.e. DMDAAC. Preferably at least 50% of the monomer units of formula (I), more preferably at least 80%, more preferably at least 90%, most preferably substantially 100% are DMDAAC units.

[0027] For the avoidance of doubt, it should be noted that the DMDAAC unit can also exist in the polymer in the form

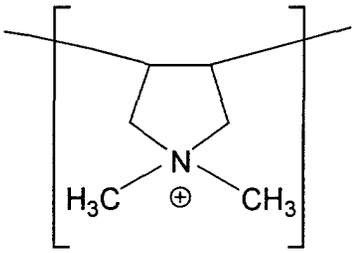


i.e. where the second allyl group remains unsaturated and does not form a ring closing bridging group constituted by groups R^2 and R^4 of formula (I). The double bond of this allyl group can also cross-link with other polymers in the sample and it can also form block co-polymers comprising the monomer unit $-CH_2-CH_2-CH_2-(CH_3)_2N^+-CH_2-CH_2-CH_2-$. Thus, polymers formed of monomer units of formula (I) in which any of R^1-R^3 is/are alkenyl groups may contain monomers with any one or more of the aforementioned structural transformations, including ring-closures, cross linking, block co-polymer formations, as well as the unpolymerised terminal unsaturated groups.

[0028] Thus, for example, where R^2 and R^4 together form a linking group R^5 by virtue of breakage of a double bond when R^2 is C_{2-4} alkenyl, the resultant monomer unit may be represented thus:-



[0029] For the example of the DMDAAC monomer unit mentioned above, the corresponding cyclic structure would therefore be:



[0030] In the case of copolymers, a wide range of other monomer units may be used, for example selected from those derived from unsaturated monocarboxylic acids such as acrylic acid, methacrylic acid, crotonic acid and the like, and their esters and salts, olefins such as ethylene, propylene and butene, alkyl esters of unsaturated carboxylic acids such as methylacrylate, ethylacrylate, methylmethacrylate, their hydroxy derivatives such as 2-hydroxyethylmethacrylate, unsaturated aromatic compounds such as styrene, methyl styrene, vinyl styrene, and heterocyclic compounds such as vinylpyrrolidone. However, most preferred are $-CH_2-CH_2-$ co-monomer units.

[0031] The monomer units of formula (I) are cationic. Optionally one or more other cationic monomer units may also be incorporated. For example, these may be chosen from any other cationic monomer unit structures disclosed in JP-A-07 316 590.

[0032] Preferably, the proportion of all cationic monomer units in the total polymer is from 40 mol % to 95 mol %, in order for the polymers to have adequate water-solubility.

[0033] It is preferred that the weight average molecular weight of the polymer is from 320 to 10,000,000, more preferably from 5,000 to 500,000, most preferably from 50,000 to 150,000. This weight average molecular weight is typically determined by the method of laser light scattering in combination with gel permeation chromatography (GPC).

[0034] In formula (I), counter anions X- may be the same of different and may include mixtures of such anions. They may for example be halide ions such as chloride or bromide, SO_4^{2-} or $CH_3SO_4^-$.

[0035] The amount of polymer in composition with other ingredients as are typically used for wash and/or rinse products may for example be from 0.05% to 10% by weight of the total composition. This level will usually be higher for rinse cycle products than for main wash products. For the latter, levels of from 0.05% to 5% by weight are typical. For the former, 1% to 10% by weight would be typical.

Synthesis of the Polymer

[0036] Many polymers based on DMDAAC and analogous monomer units are commercially available. However, formula (I) also embraces monomer units, polymers of which cannot be obtained commercially. The detergency enhancing polymers utilised in the present invention may be obtained from polymerisation of respective monomers corresponding to the monomer unit of formula (I), optionally other cationic monomer units and optionally, any other, e.g. neutral (uncharged), monomer units, each respectively being ethylenically unsaturated. The different available means of copolymerising such ethylenically unsaturated monomers will be well known to those skilled in the art of polymer chemistry. Depending on the order of addition of reactants, the resulting polymers may be block, random or mixed block/random copolymers.

Surfactants

[0037] The detergency enhancing polymer is preferably delivered in a composition which preferably comprises one or more surfactants suitable for use in laundry wash and/or rinsing products. In the most general sense, these may be chosen from one or more of soap and non-soap anionic, cationic, nonionic. amphoteric and zwitterionic surface-active compounds and mixtures thereof. Many suitable surface-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

[0038] The total level of all surfactant(s) in the composition as a whole may for example be from 0.1% to 70% by weight the total composition but is preferably from 5% to 40%.

A. Surfactants for Laundry Washing

[0039] For those compositions intended as laundry wash products, preferably, the surfactant(s) is/are selected from one or more soaps and synthetic non-soap anionic and non-ionic compounds. Detergent compositions suitable for use

in most automatic fabric washing machines generally contain anionic non-soap surfactant, or non-ionic surfactant, or combinations of the two in any suitable ratio, optionally together with soap. However, for laundry wash compositions containing the detergency enhancing polymer, it is especially preferred for these compositions to at least contain anionic surfactant.

Anionic Surfactant

[0040] In general, any anionic surfactant in compositions for use according to the present invention may comprise one or more soap and non-soap anionic surfactant materials e.g. selected from one or more of the types disclosed in the aforementioned reference of Schwartz, Perry and Berch.

[0041] Preferably, the mole ratio of total anionic surfactant to the total of all cationic monomer units in the detergency enhancing polymer is greater than 1 : 1, preferably at least more than 2.5 : 1, more preferably from 25 : 1 to 2.5 : 1, still more preferably from 20 : 1 to 3 : 1, especially from 10 : 1 to 5 : 1.

[0042] In anionic-containing compostions, the applicants have found that fatty/oily soil removal is especially effective if the hydrophobic moiety of the anionic surfactant is branched.

[0043] Typically, the branched anionic surfactant represents from 30% to 100% by weight of the total anionic surfactant, preferably from 40% to 70%. It is also preferred if the level of branched anionic surfactant is from 0.5 wt% to 30 wt%, more preferably 1 wt% to 25 wt%, most preferably from 2 wt% to 20 wt% of the total composition. Preferably, the branched anionic surfactant comprises at least one surfactant compound of formula (II)-

$$R^1 - Z^- M^+ \qquad \text{(II)}$$

wherein

R^1 is a branched hydrophobic group;

Z^- is a hydrophilic anion; and

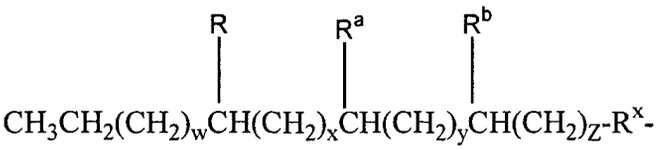
M^+ is a counter cation, preferably an alkali metal ion such as sodium.

[0044] In Formula (II), preferably, R^1 is a branched group selected from branched alkyl, alkylaryl (e.g. alkylbenzene or alkylnaphthyl) and alkenyl groups most preferably having from 6 to 24 carbon atoms in the aliphatic part thereof.

[0045] Preferably also, Z- represents a sulphate, sulphonate, carboxylate or phosphonate group, any at which is optionally linked to R^1 via a linking moiety, such as (poly) C_{2-4} alkyleneoxy moiety, forming part of Z-. In the latter example (when present) preferably there may for example be from 1 to 7 alkyleneoxy groups (which may be the same or different) and which are preferably selected from alkyleneoxy and/or propyleneoxy groups.

[0046] As all or part (e.g at least 50%, 60%, 70%, 80%, 90% or 95% by weight) of the branched anionic surfactant component, most preferred are the linear alkylbenzene sulphonate anionic surfactants having an average alkyl component of C_8-C_{15}, especially those having a V-shaped hydrophobe group R^1, i.e. branching at the point of attachment to the benzene sulphonate group but each arm of the V is linear. Commercial products contain a mixture of different chain lengths for each arm length. Paradoxically, such V- branched materials are sometimes referred to as "linear" alkylbenzene sulphonates.

[0047] Another preferred class of branched anionic surfactant comprises those disclosed in WO-A-99/19428 in which R^1 is attached to the Z- moiety via a group $-R^x-$ (wherein R^x is absent or is a linking group such as phenylene), R^1 being a hydrophobic mid-chain branched alkyl moiety, having in total 9 to 22 carbons in the moiety, preferably from 12 to about 18, having: (1) a longest linear carbon chain attached to the $-R^x-Z^-$ moiety in the range of from 8 to 21 carbon atoms; (2) one or more C_1 - C_3 alkyl moieties branching from this longest linear carbon chain; (3) at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of the position 2 carbon, counting from position 1 carbon (#1) which is attached to the $-R^x-Z-$ moiety, to the position of the terminal carbon minus 2 carbons, (the (ω - 2) carbon); and (4) when more than one of these compounds is present, the average total number of carbon atoms in the R^1-R^x- moieties in the above formula is within the range of greater than 14.5 to about 18, preferably from about 15 to about 17. Preferred R^1 groups as defined in WO-A-99/19428 are branched primary alkyl moieties having the formula:



wherein the total number of carbon atoms in the branched primary alkyl moiety of this formula (including the R, R^a, and R^b branching) is from 13 to 19; R, R^x is as hereinbefore defined R^a, and R^b are each independently selected from hydrogen and C_1-C_3 alkyl (preferably methyl), provided R, R^a, and R^b are not all hydrogen and, when z is 0, at least R or R^a is not hydrogen; w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer from 0 to 13; and w + x + y + z is from 7 to 13.

[0048] Yet other suitable branched anionic surfactants include secondary alkylsulphonates, secondary alcohol sulphates and secondary alkyl carboxylates.

[0049] The laundry wash compositions of the invention may additionally or alternatively contain one or more other anionic surfactants in total amounts corresponding to percentages quoted above for linear alkyl benzene sulphonates, provided that at least some branched anionic surfactant is present. Suitable anionic surfactants are well-known to those skilled in the art. These include primary alkyl sulphates, particularly C_8-C_{15} primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred. Such other anionic surfactants typically are used at from 5% to 70% by weight of the total anionic surfactant, preferably from 10% to 30%. Moreover, they typically represent from 1% to 15% by weight of the total composition.

Nonionic Surfactants

[0050] The compositions for use of the polymer according to the invention preferably also contain nonionic surfactant. Nonionic surfactants that may be used include fatty acid methyl ester ethoxylates (FAMEE's), e.g. as supplied by Lion Corp., Henkel KGA, Condea or Clairant, the primary and secondary alcohol ethoxylates, especially the C_8-C_{20} aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C_{10}-C_{15} primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

[0051] It is preferred if the level of total non-ionic surfactant is from 0 wt% to 30 wt%, preferably from 1 wt% to 25 wt%, most preferably from 2 wt% to 15 wt% by weight of the total composition.

Other Surfactants

[0052] Another class of suitable surfactants comprises certain mono-long chain-alkyl cationic surfactants for use in main-wash laundry compositions according to the invention. Cationic surfactants of this type include quaternary ammonium salts of the general formula $R_1R_2R_3R_4N^+$ X- wherein the R groups are long or short hydrocarbon chains, typically alkyl, hydroxyalkyl or ethoxylated alkyl groups, and X is a counter-ion (for example, compounds in which R_1 is a C_8-C_{22} alkyl group, preferably a C_8-C_{10} or C_{12}-C_{14} alkyl group, R_2 is a methyl group, and R_3 and R_4, which may be the same or different, are methyl or hydroxyethyl groups); and cationic esters (for example, choline esters).

[0053] The choice of surface-active compound (surfactant), and the amount present in the laundry wash compositions according to the invention, will depend on the intended use of the detergent composition. In fabric washing compositions, different surfactant systems may be chosen, as is well known to the skilled formulator, for handwashing products and for products intended for use in different types of washing machine. The total amount of surfactant present will also depend on the intended end use and may be as high as 60 wt%, for example, in a composition for washing fabrics by hand. In compositions for machine washing of fabrics, an amount of from 5 to 40 wt% is generally appropriate. Typically the compositions will comprise at least 2 wt% surfactant e.g. 2-60%, preferably 15-40% most preferably 25-35%.

Surfactant Blends

[0054] Preferred blends for laundry wash products comprise the anionic surfactant(s) and one or more nononic surfactants. Compositions suitable for use in most automatic fabric washing machines will generally contain anionic non-

soap surfactant, or non-ionic surfactant, or combinations of the two in any suitable ratio, optionally together with soap. Typical blends contain total anionic to total nonionic surfactant in a weight ratio of from 5 : 1 to 1 : 1, preferably from 4 : 1 to 2 : 1.

B. Surfactant for Rinse Products

[0055] In the case of laundry rinse compositions containing the detergency enhancing polymer for use according to the invention, the surfactant(s) is/are preferably selected from fabric conditioning agents. In fact, conventional fabric conditioning agent may be used. These conditioning agents may be cationic or non-ionic. If the fabric conditioning compound is to be employed in a main wash detergent composition the compound will typically be non-ionic. If used in the rinse phase, they will typically be cationic. They may for example be used in amounts from 0.5% to 35%, preferably from 1% to 30% more preferably from 3% to 25% by weight of the composition.

[0056] Preferably the fabric conditioning agent(s) have two long chain alkyl or alkenyl chains each having an average chain length greater than or equal to C_{16}. Most preferably at least 50% of the long chain alkyl or alkenyl groups have a chain length of C_{18} or above.

[0057] It is preferred if the long chain alkyl or alkenyl groups of the fabric conditioning agents are predominantly linear.

[0058] The fabric conditioning agents are preferably compounds that provide excellent softening, and are characterised by a chain melting L_β to L_α transition temperature greater than 25°C, preferably greater than 35°C, most preferably greater than 45°C. This L_β to L_α transition can be measured by DSC as defined in " Handbook of Lipid Bilayers, D Marsh, CRC Press, Boca Raton, Florida, 1990 (pages 137 and 337).

[0059] Substantially insoluble fabric conditioning compounds in the context of this invention are defined as fabric conditioning compounds having a solubility less than 1×10^{-3} wt % in demineraliised water at 20°C. Preferably the fabric softening compounds have a solubility less than 1×10^{-4} wt %, most preferably less than 1×10^{-8} to 1×10^{-6}. Preferred cationic fabric softening agents comprise a substantially water insoluble quaternary ammonium material comprising a single alkyl or alkenyl long chain having an average chain length greater than or equal to C_{20} or, more preferably, a compound comprising a polar head group and two alkyl or alkenyl chains having an average chain length greater than or equal to C_{14}.

[0060] Preferably, the cationic fabric softening agent is a quaternary ammonium material or a quaternary ammonium material containing at least one ester group. The quaternary ammonium compounds containing at least one ester group are referred to herein as ester-linked quaternary ammonium compounds.

[0061] As used in the context of the quarternary ammonium cationic fabric softening agents, the term 'ester group', includes an ester group which is a linking group in the molecule.

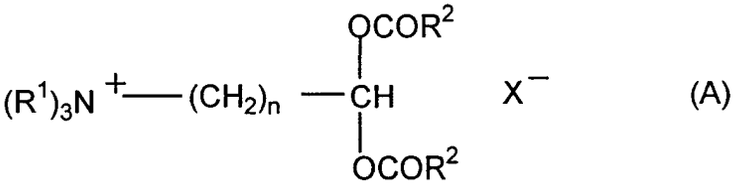
[0062] It is preferred for the ester-linked quaternary ammonium compounds to contain two or more ester groups. In both monoester and the diester quaternary ammonium compounds it is preferred if the ester group(s) is a linking group between the nitrogen atom and an alkyl group. The ester groups(s) are preferably attached to the nitrogen atom via another hydrocarbyl group.

[0063] Also preferred are quaternary ammonium compounds containing at least one ester group, preferably two, wherein at least one higher molecular weight group containing at least one ester group and two or three lower molecular weight groups are linked to a common nitrogen atom to produce a cation and wherein the electrically balancing anion is a halide, acetate or lower alkosulphate ion, such as chloride or methosulphate. The higher molecular weight substituent on the nitrogen is preferably a higher alkyl group, containing 12 to 28, preferably 12 to 22, e.g. 12 to 20 carbon atoms, such as coco-alkyl, tallowalkyl, hydrogenated tallowalkyl or substituted higher alkyl, and the lower molecular weight substituents are preferably lower alkyl of 1 to 4 carbon atoms, such as methyl or ethyl, or substituted lower alkyl. One or more of the said lower molecular weight substituents may include an aryl moiety or may be replaced by an aryl, such as benzyl, phenyl or other suitable substituents.

[0064] Preferably the quaternary ammonium material is a compound having two C_{12}-C_{22} alkyl or alkenyl groups connected to a quaternary ammonium head group via at least one ester link, preferably two ester links or a compound comprising a single long chain with an average chain length equal to or greater than C_{20}.

[0065] More preferably, the quaternary ammonium material comprises a compound having two long chain alkyl or alkenyl chains with an average chain length equal to or greater than C_{14}. Even more preferably each chain has an average chain length equal to or greater than C_{16}. Most preferably at least 50% of each long chain alkyl or alkenyl group has a chain length of C_{18}. It is preferred if the long chain alkyl or alkenyl groups are predominantly linear.

[0066] The most preferred type of ester-linked quaternary ammonium material that can be used in laundry rinse compositions according to the invention is represented by the formula (A):



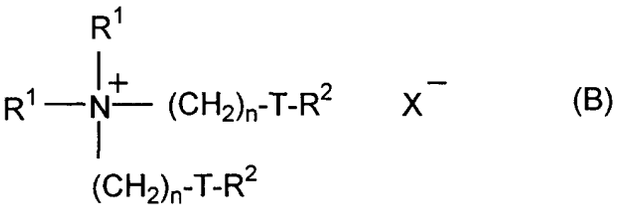
wherein each R^{20} group is independently selected from C_{1-4} alkyl, hydroxyalkyl or C_{2-4} alkenyl groups; and wherein each R^{21} group is independently selected from C_{8-28} alkyl or alkenyl groups; Y^- is any suitable counter-ion, i.e. a halide, acetate or lower alkosulphate ion, such as chloride or methosulphate; and w is an integer from 1-5 or is 0.

[0067] It is especially preferred that each R^{20} group is methyl and each w is 2.

[0068] It is advantageous for environmental reasons if the quaternary ammonium material is biologically degradable.

[0069] Preferred materials of this class such as 1,2 bis[hardened tallowoyloxy]-3-trimethylammonium propane chloride and their method of preparation are, for example, described in US-A-4 137 180. Preferably these materials comprise small amounts of the corresponding monoester as described in US-A-4 137 180 for example 1-hardened tallowoyloxy-2-hydroxy-3-trimethylammonium propane chloride.

[0070] Another class of preferred ester-linked quaternary ammonium materials for use in laundry rinse compositions according to the invention can be represented by the formula(B):

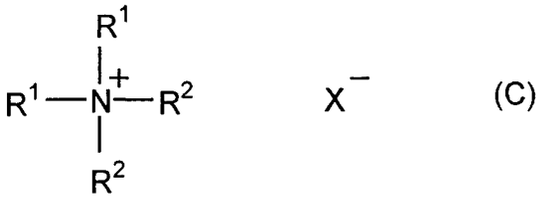


wherein

T is -O-C(O)- or -C(O)-O- ; and
wherein R^{20}, R^{21}, w, and Y^- are as defined above.

[0071] Of the compounds of formula (B), di-(tallowyloxyethyl)-dimethyl ammonium chloride, available from Hoechst, is the most preferred. Di-(hardened tallowyloxyethyl)dimethyl ammonium chloride, ex Hoechst and di-(tallowyloxyethyl)-methyl hydroxyethyl methosulphate are also preferred.

[0072] Another preferred class of quaternary ammonium cationic fabric softening agent is defined by formula (C):-



where R^{20}, R^{21} and Y^- are as hereinbefore defined.

[0073] A preferred material of formula (C) is di-hardened tallow-diethyl ammonium chloride, sold under the Trademark Arquad 2HT.

[0074] The optionally ester-linked quaternary ammonium material may contain optional additional components, as known in the art, in particular, low molecular weight solvents, for instance isopropanol and/or ethanol, and co-actives such as nonionic softeners, for example fatty acid or sorbitan esters.

Further Optional Ingredients

[0075] Compositions containing the detergency enhancing polymer for use according to the invention, optionally contain one or more other ingredients. In other words, these other ingredients do not have to be present. Preferably however, there compositions according to the invention contain one or more other ingredients typically found in laundry wash products. Preferably, these are selected from one or more of surfactants (other than the anionic surfactant), builders, bleaches, enzymes and minor ingredients.

Detergency Builders

[0076] The compositions for use of the polymer in accordance with the invention, when used as laundry wash compositions, will generally also contain one or more detergency builders. The total amount of detergency builder in the compositions will typically range from 5 to 80 wt%, preferably from 10 to 60 wt% by weight of the total composition. As already explained above, many laundry wash compositions contain one or more anionic surfactants and when present, it is especially preferred that at least some of the anionic surfactant(s) present comprise one or more branched anionic surfactants. When anionic surfactant is included in such compositions, it is preferred for the weight ratio of total anionic surfactant of total builder to be from 1:10 to 10:1, more preferably from 2:1 to 10:1, still more preferably from 3:1 to 7:1; and independently of these ratios, it is preferred that the weight ratio of total branched surfactant to total builder is from 1:5 to 10:1, preferably from 1:1 to 7:1.

[0077] Inorganic builders that may be present include sodium carbonate, if desired in combination with a crystallisation seed for calcium carbonate, as disclosed in GB-A-1 437 950; crystalline and amorphous aluminosilicates, for example, zeolites as disclosed in GB-A-1 473 201, amorphous aluminosilicates as disclosed in GB-A-1 473 202 and mixed crystalline/amorphous aluminosilicates as disclosed in GB-A-1 470 250; and layered silicates as disclosed in EP-A-164 514. Inorganic phosphate builders, for example, sodium orthophosphate, pyrophosphate and tripolyphosphate are also suitable for use with this invention.

[0078] The compositions of the invention preferably contain an alkali metal, preferably sodium, aluminosilicate builder. Sodium aluminosilicates may generally be incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50 wt%.

[0079] The alkali metal aluminosilicate may be either crystalline or amorphous or mixtures thereof, having the general formula: 0.8-1.5 Na_2O. Al_2O_3. 0.8-6 SiO_2.

[0080] These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units (in the formula above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1 429 143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.

[0081] The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. However, according to a preferred embodiment of the invention, the zeolite builder incorporated in the compositions of the invention is maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP-A-384 070. Zeolite MAP is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.

[0082] Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.

[0083] Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di and trisuccinates, carboxymethyloxy succinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts. This list is not intended to be exhaustive.

[0084] Especially preferred organic builders are citrates, suitably used in amounts of from 5 to 30 wt%, preferably from 10 to 25 wt%; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, preferably from 1 to 10 wt%.

[0085] Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

Bleaches

[0086] Laundry wash compositions containing the detergency enhancing polymer for use according to the invention may also suitably contain a bleach system. Fabric washing compositions may desirably contain peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, capable of yielding hydrogen peroxide in aqueous

solution.

[0087] Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate.

[0088] Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture. Sodium percarbonate having a protective coating comprising sodium metaborate and sodium silicate is disclosed in GB-A-2 123 044.

[0089] The peroxy bleach compound is suitably present in an amount of from 0.1 to 35 wt%, preferably from 0.5 to 25 wt%. The peroxy bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 0.1 to 8 wt%, preferably from 0.5 to 5 wt%.

[0090] Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors and pernoanoic acid precursors. Especially preferred bleach precursors suitable for use in the present invention are N,N,N',N',-tetracetyl ethylenediamine (TAED) and sodium noanoyloxybenzene sulphonate (SNOBS). The novel quaternary ammonium and phosphonium bleach precursors disclosed in US 4 751 015 and US-A-4 818 426 and EP-A-402 971, and the cationic bleach precursors disclosed in EP-A-284 292 and EP-A-303 520 are also of interest.

[0091] The bleach system can be either supplemented with or replaced by a peroxyacid. examples of such peracids can be found in US-A- 4 686 063 and US-A- 5 397 501. A preferred example is the imido peroxycarboxylic class of peracids described in EP-A-325 288, EP-A-349 940, DE-A-382 3172 and EP-A-325 289. A particularly preferred example is phtalimido peroxy caproic acid (PAP). Such peracids are suitably present at 0.1 - 12%, preferably 0.5 - 10%.

[0092] A bleach stabiliser (transition metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetra-acetate (EDTA), the polyphosphonates such as Dequest (Trade Mark) and non-phosphate stabilisers such as EDDS (ethylene diamine di-succinic acid). These bleach stabilisers are also useful for stain removal especially in products containing low levels of bleaching species or no bleaching species.

[0093] An especially preferred bleach system comprises a peroxy bleach compound (preferably sodium percarbonate optionally together with a bleach activator), and a transition metal bleach catalyst as described and claimed in EP-A-458 397, EP-A-458 398 and EP-A-509 787.

Enzymes

[0094] Laundry wash compositions according to the invention may also contain one or more enzyme(s). Suitable enzymes include the proteases, amylases, cellulases, oxidases, peroxidases and lipases usable for incorporation in detergent compositions. Preferred proteolytic enzymes (proteases) are, catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis reaction. They may be of any suitable origin, such as vegetable, animal, bacterial or yeast origin.

[0095] Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available and can be used in the instant invention. Examples of suitable proteolytic enzymes are the subtilisins which are obtained from particular strains of B. Subtilis B. licheniformis, such as the commercially available subtilisins Maxatase (Trade Mark), as supplied by Gist Brocades N.V., Delft, Holland, and Alcalase (Trade Mark), as supplied by Novo Industri A/S, Copenhagen, Denmark.

[0096] Particularly suitable is a protease obtained from a strain of Bacillus having maximum activity throughout the pH range of 8-12, being commercially available, e.g. from Novo Industri A/S under the registered trade-names Esperase (Trade Mark) and Savinase (Trade-Mark). The preparation of these and analogous enzymes is described in GB 1 243 785. Other commercial proteases are Kazusase (Trade Mark obtainable from Showa-Denko of Japan), Optimase (Trade Mark from Miles Kali-Chemie, Hannover, West Germany), and Superase (Trade Mark obtainable from Pfizer of U.S.A.).

[0097] Detergency enzymes are commonly employed in granular form in amounts of from about 0.1 to about 3.0 wt%. However, any suitable physical form of enzyme may be used.

Other Optional Minor Ingredients

[0098] The compositions of the invention may contain alkali metal, preferably sodium carbonate, in order to increase detergency and ease processing. Sodium carbonate may suitably be present in amounts ranging from 1 to 60 wt%, preferably from 2 to 40 wt%. However, compositions containing little or no sodium carbonate are also within the scope of the invention.

[0099] Powder flow may be improved by the incorporation of a small amount of a powder structurant, for example, a fatty acid (or fatty acid soap), a sugar, an acrylate or acrylate/maleate copolymer, or sodium silicate. One preferred powder structurant is fatty acid soap, suitably present in an amount of from 1 to 5 wt%.

[0100] Yet other materials that may be present in detergent compositions of the invention include sodium silicate; antiredeposition agents such as cellulosic polymers; inorganic salts such as sodium sulphate; lather control agents or lather boosters as appropriate; dyes; coloured speckles; perfumes; foam controllers; fluorescers and decoupling polymers. This list is not intended to be exhaustive.

Product Form

[0101] Compositions containing the detergency enhancing polymer for use according to the present invention may be formulated in any convenient form, for example as powders, liquids (aqueous or non-aqueous) or tablets.

[0102] Particulate detergent compositions are suitably prepared by spray-drying a slurry of compatible heat-insensitive ingredients, and then spraying on or post-dosing those ingredients unsuitable for processing via the slurry. The skilled detergent formulator will have no difficulty in deciding which ingredients should be included in the slurry and which should not.

[0103] Particulate detergent compositions of the invention preferably have a bulk density of at least 400 g/1, more preferably at least 500 g/1. Especially preferred compositions have bulk densities of at least 650 g/litre, more preferably at least 700 g/litre.

[0104] Such powders may be prepared either by post-tower densification of spray-dried powder, or by wholly non-tower methods such as dry mixing and granulation; in both cases a high-speed mixer/granulator may advantageously be used. Processes using high-speed mixer/granulators are disclosed, for example, in EP-A-340 013, EP-A-367 339, EP-A-390 251 and EP-A-420 317.

[0105] Liquid detergent compositions according to the invention can be prepared by admixing the essential and optional ingredients thereof in any desired order to provide compositions containing components in the requisite concentrations. Liquid compositions according to the present invention can also be in compact form which means it will contain a lower level of water compared to a conventional liquid detergent.

[0106] Tablet compositions according to the invention may for example be prepared by mixing a base powder comprising the anionic surfactant, the polymer of formula (I) and other optional ingredients and tabletting the base powder in a Carver hand press to form cylindrical tablets of approximately 44 mm diameter, as described in WO-A-98/42817 and WO-A-99/20730.

[0107] The present invention will now be explained in more detail by way of the following non-limiting examples.

Examples

[0108]

Example	**A**	**1**	**2**	**B**	**3**	**4**	**C**	**5**	**6**
NaLAS [1]	13	12.35	11.7	13	12.35	11.7	6	5.7	5.4
Nonionic [2]	-	-	-	13	13	13	7	7	7
STP [3]	23	23	23	23	23	23	-	-	-
Zeolite[4]	-	-	-	-	-	-	22	22	22
Na_2CO_3	10	10	10	10	10	10	-	-	-
Na disilicate	6	6	6	6	6	6	-	-	-
Polymer [5]	-	0.65	1.3	-	0.65	1.3	-	0.3	0.6
NaLAS: Polymer	-	19:1	9:1	-	19:1	9:1	-	19:1	9:1

1. C_{11-12} alkylbenzene sulphonate, sodium salt
2. Nonionic surfactant having an average of from 3 to 7 ethylene oxide units per mole, and an alkyl chain length of from 9 to 15 carbon atoms.
3. Sodium tripolyphosphate
4. Zeolite 24, aluminosilicate builder
5. Poly-DMDAAC, wt. av. MW = 100,000 as determined by GPC.

[0109] In the following evaluation results, the compositions were in all cases dosed at 5.0g/l. The wash regime was 30 minutes washing in 17° FH water hardness.

[0110] In a laboratory scale wash evaluation (LWE) simulating a machine wash, examples A and 1 were tested for washing performance with cotton soiled with kitchen grease and examples A, and 2 were tested in a minibottle (MBT) test for each performance with cotton collars and cuffs stained with sebum.

	Reflectance Units (RU)	
Example	**LWE**	**MBT**
A	15.2	14.1
1	15.4	-
2	-	15.1

[0111] Examples B, 3 and 4 were compared in an LWE test for performance in removing olive oil and carbon back staining on cotton.

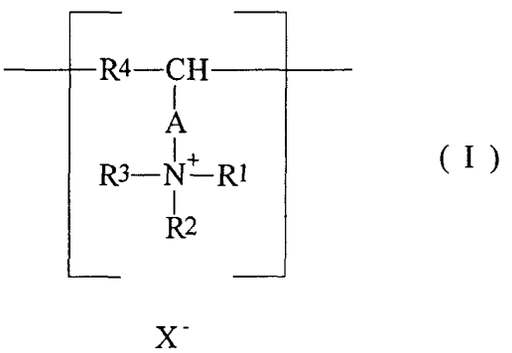
Example	RU
B	2.6
3	2.7
4	2.9

[0112] Examples C, 5 and 6 were compared in a MBT test for performance against sebum soiling of cotton collars and cuffs.

Example	RU
C	14.0
5	15.4
6	14.9

Claims

1. Use of a detergency enhancing polymer in a laundry cleaning operation to improve removal of oily and/or greasy soil from cotton fabrics, said detergency enhancing polymer being a homopolymer or copolymer containing one or more monomer units independently selected from those of formula (I)



(I)

wherein

-A- is selected from groups of formula $-R^5-$, $-R^5-(CO)-R^6-$, $-R^5-(CO)-O-R^6$, $-R^5-O-(CO)-R^6-$, $-R^5-(CO)-NH-R^6-$, $-R^5-NH-(CO)-R^6-$, wherein R^5 and R^6 are independently absent, or represent C_{1-3} alkyl groups;

R^1, R^2 and R^3 are independently selected from hydrogen, C_{1-3} alkyl, C_{1-3} alkenyl, hydroxy-C_{1-3} alkyl and C_{5-8} cycloalkyl groups; and

R^4 is selected from groups as defined for A above;

wherein R^3 may also represent a bridging group to the group R^4, said bridging group being selected from groups as defined for A above; and

X - is a monovalent anion or an n'th part of an n-valent anion.

2. Use according to claim 1, wherein in at least some of unit(s) of formula (I), A is methylene or carbonyl and R^4 is methylene or ethylene.

3. Use according to claim 1, wherein in at least some of the monomer units of formula (I), A is methylene, R^1 and R^2 are both methyl, and R^3 and R^4 together represent -(CH-)-CH_2-, or structural variants thereof.

4. Use according to any preceding claim, wherein the molar average of monomer units of formula (I) comprise at least 50% of the monomer units as defined in claim 3, preferably at least 90% and more preferably substantially 100%.

5. Use according to any preceding claim, wherein the polymer contains at least 40 mole % of cationic monomer units in the total polymer.

6. Use according to any preceding claim, wherein the weight average molecular weight of the polymer is from 320 to 10,000,000, preferably from 5,000 to 500,000, more preferably from 50,000 to 150,000.

7. Use according to any preceding claim, wherein the detergency enhancing polymer is incorporated in a composition which also comprises surfactant and optionally, one or more further ingredients.

8. Use according to claim 7, wherein the surfactant comprises at least some anionic surfactant.

9. Use according to claim 8, wherein the mole ratio of anionic surfactant to the total of all cationic monomer units in the detergency enhancing polymer is greater than 1 : 1, preferably at least 2.5 : 1, preferably from 25 : 1 to 2.5: 1, still more preferably from 20 : 1 to 3 : 1, especially from 10:1 to 5 : 1.

10. Use according to claim 8 or claim 9, according to any preceding claim, wherein the anionic surfactant comprises from 0.5% to 30%, preferably from 1% to 25%, more preferably from 2% to 20% by weight of the total composition of branched anionic surfactant.

11. Use according to any of claims 8-10, wherein the anionic surfactant comprises from 30% to 100%, preferably from 40% to 70%, of branched anionic surfactant based on the weight of total anionic surfactant.

12. Use according to any of claims 8-11, wherein the composition further comprises from 0% to 30%, preferably from 1% to 25%, more preferably from 2% to 15% by weight of the total composition, of nonionic surfactant.

13. Use according to claim 12, wherein the weight ratio of total anionic surfactant to total nonionic surfactant is from 5 : 1 to 1 : 1, preferably from 4 : 1 to 2 : 1.

14. Use according to any of claims 8-13, wherein the composition further comprises from 5% to 80%, preferably from 10% to 60% by weight of the total composition of detergency builder.

15. Use according to any of claims 8-14, wherein the composition comprises from 0.05 to 5% by weight of detergency enhancing polymer .

16. Use according to any of claims 1-7, wherein the detergency enhancing polymer is incorporated in a composition which comprises at least one fabric conditioning cationic and/or nonionic surfactant.

17. Use according to claim 16, wherein the amount of fabric conditioning surfactant is from 0.3% to 35%, preferably from 1% to 30%, more preferably from 3% to 25% by weight of the total composition.

18. Use according to claim 17, wherein the composition comprises from 0.1% to 10% by weight of detergency en-

hancing polymer.