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(54) **HYDROPHOBICALLY MODIFIED
POLYALKYLENIMINES FOR USE AS DYE
TRANSFER INHIBITORS**

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(57) **ABSTRACT**

The invention relates to the use of hydrophobically modified polyalkylenimines as dye transfer inhibitors.

HYDROPHOBICALLY MODIFIED POLYALKYLENIMINES FOR USE AS DYE TRANSFER INHIBITORS

[0001] The invention relates to the use of hydrophobically modified polyalkylenimines as dye transfer inhibitors.

[0002] During the washing process, dye molecules are often detached from colored textiles; these can in turn attach to other textiles. In order to counteract this undesired dye transfer, so-called dye transfer inhibitors are often used. These are frequently polymers which comprise monomers with nitrogen-heterocyclic radicals in copolymerized form.

[0003] Thus, for example, DE 4235798 describes copolymers of 1-vinylpyrrolidone, 1-vinylimidazole, 1-vinylimidazolium compounds or mixtures thereof; further nitrogen-containing, basic ethylenically unsaturated monomers; and, if appropriate, other monoethylenically unsaturated monomers and their use for inhibiting dye transfer during the washing process.

[0004] Similar copolymers are described for this purpose in DE 19621509 and WO 98/30664.

[0005] The copolymers described in these specifications are characterized in part by good inhibition of dye transfer in washing processes. However, they generally have poor compatibility with the other detergent constituents customarily used. Thus, particularly in the case of liquid detergents, there is the danger of incompatibilities, for example in the form of opacity or phase separations.

[0006] On several occasions, the use of hydrophobically modified polyalkylenimines in detergent and cleaner formulations has been described.

[0007] DE 2025829 describes reaction products of fatty acid glycidyl esters with polyethylenimines and their use as fabric softeners.

[0008] DE 2046304 describes reaction products of fatty acids or fatty acid esters with polyethylenimines and their use as fabric softeners.

[0009] DE 2165900 describes reaction products of alkyl glycidyl ethers with polyethylenimines and their use as gray-ing inhibitors.

[0010] U.S. Pat. No. 3,576,341 describes alkylated polyethylenimines in which the alkyl groups have 16 to 30 carbon atoms, and use as fabric softeners.

[0011] WO 2002/095122 describes the use of hydrophobically modified polyethylenimines as antirelease additives for detergent formulations.

[0012] An effect of the hydrophobically modified polyalkylenimines inhibiting dye transfer during washing is described in none of these citations.

[0013] It was an object of the present invention to provide substances with a good dye transfer-inhibiting effect during the washing process. These substances should additionally have good compatibility with conventional detergent constituents, especially in the case of liquid detergent formulations.

[0014] These and further objects are surprisingly achieved through hydrophobically modified poly-C₂-C₄-alkylenimines.

[0015] The invention therefore relates to the use of hydrophobically modified poly-C₂-C₄-alkylenimines, in particular hydrophobically modified polyethylenimines, as dye transfer inhibitors in detergent compositions for textiles.

[0016] Here and in what follows, hydrophobically modified poly-C₂-C₄-alkylenimines are to be understood as meaning poly-C₂-C₄-alkylenimines in which the hydrogen atoms of the primary and secondary amino groups are partially or completely replaced by linear or branched aliphatic, saturated or unsaturated hydrocarbon radicals such as alkyl, alkenyl, alkadienyl or hydroxyalkyl radicals. The hydrocarbon radicals generally have at least 8, e.g. 8 to 30, carbon atoms, preferably 10 to 22 carbon atoms, in particular 10 to 18 carbon atoms.

[0017] Depending on the hydrophobicizing agent used in each case, the hydrocarbon radicals can be linked to the nitrogen atom of the poly-C₂-C₄-alkylenimine directly or via a functional group, e.g. via a carbonyl group (*-C(=O)-[#]), via an oxycarbonyl group (*-O-C(=O)-[#]), via an aminocarbonyl group (*-NH-C(=O)-[#]), via a carbonyloxyhydroxypropyl group (*-C(=O)-O-CH₂-CH(OH)-CH₂-[#]), via a 2-oxycarbonylethylenecarbonyl group (*-CH(COOH)-CH₂-CO-[#]), or via a radical of the formula *-CH₂-C(=O)-CH*-C(=O)-[#] (in the formulae given above, * represents the linkage to the hydrocarbon radical and # represents the linkage to the nitrogen atom of the poly-C₂-C₄-alkylenimine). The hydrocarbon radical can also form an aldimine or ketimine group with the nitrogen of the poly-C₂-C₄-alkylenimine, or be linked to 2 nitrogen atoms of the poly-C₂-C₄-alkylenimine via the carbon atom of a cyclic amidine group.

[0018] Preference is given to those hydrophobically modified poly-C₂-C₄-alkylenimines in which the hydrocarbon radical is linked to one nitrogen atom of the poly-C₂-C₄-alkylenimine directly or via a carbonyl group, the latter being particularly preferred.

[0019] Preferably, the hydrocarbon radicals are linear. Preferably, the hydrocarbon radicals are saturated.

[0020] Accordingly, the hydrocarbon radicals in the preferred hydrophobically modified poly-C₂-C₄-alkylenimines are present in the form of C₈-C₃₀-alkyl, C₈-C₃₀-alkylcarbonyl, C₈-C₃₀-alkenyl, C₈-C₃₀-alkenylcarbonyl, C₈-C₃₀-alkadienyl, C₈-C₃₀-alkadienylcarbonyl and/or hydroxy-C₈-C₃₀-alkyl groups, in particular in the form of C₁₀-C₂₂-alkyl, C₁₀-C₂₂-alkylcarbonyl, C₁₀-C₂₂-alkenyl, C₁₀-C₂₂-alkenylcarbonyl, C₁₀-C₂₂-alkadienyl, C₁₀-C₂₂-alkadienylcarbonyl and/or hydroxy-C₁₀-C₂₂-alkyl groups, particularly preferably in the form of C₁₀-C₁₈-alkyl, C₁₀-C₁₈-alkylcarbonyl, C₁₀-C₁₈-alkenyl, C₁₀-C₁₈-alkenylcarbonyl, C₁₀-C₁₈-alkadienyl, C₁₀-C₁₈-alkadienylcarbonyl and/or hydroxy-C₁₀-C₁₈-alkyl groups, where the alkyl, hydroxy-alkyl, alkenyl, alkadienyl radicals of the aforementioned groups are preferably linear.

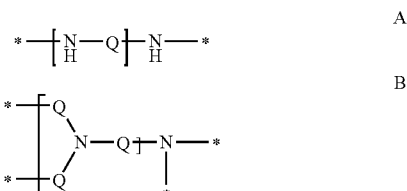
[0021] In the particularly preferred hydrophobically modified poly-C₂-C₄-alkylenimines, the hydrocarbon radicals are present in the form of C₈-C₃₀-alkylcarbonyl or C₈-C₃₀-alkenylcarbonyl groups, in particular in the form of C₁₀-C₂₂-alkylcarbonyl or C₁₀-C₂₂-alkenylcarbonyl groups and specifically in the form of C₁₀-C₁₈-alkylcarbonyl or C₁₀-C₁₈-alkenylcarbonyl groups, where the alkyl and alkenyl radicals of the aforementioned groups are preferably linear.

[0022] Preference is furthermore given to those hydrophobically modified poly-C₂-C₄-alkylenimines in which at least 10 mol %, in particular at least 15 mol % and particularly preferably at least 20 mol %, e.g. 5 to 80 mol %, in particular 15 to 70 mol % and specifically 20 to 60 mol %, of the nitrogen atoms of the poly-C₂-C₄-alkylenimine carry a hydrocarbon radical.

[0023] Correspondingly, the fraction of the hydrocarbon radicals constitutes preferably 25 to 95% by weight, in particular 30 to 90% by weight and specifically 40 to 80% by weight, based on the total weight of the hydrophobically modified poly-C₂-C₄-alkylenimine.

[0024] The weight-average molecular weight Mw of hydrophobically modified poly-C₂-C₄-alkylenimines suitable according to the invention is typically in the range from 1000 to 1 000 000 Daltons. For the use according to the invention, it has furthermore proven advantageous if the hydrophobically modified poly-C₂-C₄-alkylenimine has a number-average molecular weight in the range from 3000 to 300 000 Daltons and in particular in the range from 6000 to 200 000 Daltons. The molecular weights given here refer to the molecular weights specified by means of dynamic light scattering and measured on dilute aqueous solutions at 25° C. which correspond to the weight-average molecular weight.

[0025] The hydrophobically modified poly-C₂-C₄-alkylenimines used according to the invention, in particular the hydrophobically modified polyethylenimines, can, based on the poly-C₂-C₄-alkylenimine on which they are based, be linear or branched, preference being given to those which are branched in the poly-C₂-C₄-alkylenimine moiety. Whereas linear poly-C₂-C₄-alkylenimines are composed exclusively of repeat units of formula A, in which Q is C₂-C₄-alkylene, branched poly-C₂-C₄-alkylenimines have, besides the linear repeat units, tertiary nitrogen atoms according to the structural unit B:



[0026] Preference is given to those branched, hydrophobically modified poly-C₂-C₄-alkylenimines, in particular branched, hydrophobically modified polyethylenimines, which, based on the poly-C₂-C₄-alkylenimine on which they are based, have, on average, per polyalkylenimine molecule at least one, preferably at least 5 or at least 10, branching points according to formula B. In particular, at least 5%, in particular at least 10% and particularly preferably at least 15%, e.g. 5 to 40% and specifically 15 to 35%, of the nitrogen atoms of the parent poly-C₂-C₄-alkylenimine are tertiary nitrogen atoms.

[0027] Particularly in the case of relatively high degrees of branching, i.e. if at least 10%, in particular at least 15%, e.g. 10 to 40%, in particular 15 to 35% of the nitrogen atoms of the parent poly-C₂-C₄-alkylenimine are tertiary nitrogen atoms, the hydrophobically modified poly-C₂-C₄-alkylenimines have a structure similar to a core-shell structure, where the poly-C₂-C₄-alkylenimine moieties form the core and the hydrophobic radicals form the shell.

[0028] The hydrophobically modified poly-C₂-C₄-alkylenimines can be present in uncrosslinked or crosslinked form, and, besides the hydrophobic modification, may be quaternized and/or modified through reaction with alkylene oxides, di-C₁-C₄-alkyl carbonates, C₂-C₄-alkylene carbonates or C₁-C₄-carboxylic acids.

[0029] Preferably, the hydrophobically modified poly-C₂-C₄-alkylenimines are uncrosslinked.

[0030] According to a first preferred embodiment of the invention, the hydrophobically modified poly-C₂-C₄-alkylenimines have no further modification besides the hydrophobic modification.

[0031] According to a second preferred embodiment of the invention, the hydrophobically modified poly-C₂-C₄-alkylenimines are quaternized in addition to the hydrophobic modification. Such quaternized hydrophobically modified poly-C₂-C₄-alkylenimines preferably have no further modification. The degree of quaternization, i.e. the number of quaternized nitrogen atoms, based on the total amount of the nitrogen atoms of the hydrophobically modified poly-C₂-C₄-alkylenimine, is preferably not more than 80 mol %, in particular not more than 50 mol %, e.g. 1 to 80 mol %, in particular 5 to 50 mol %, based on the nitrogen atoms of the poly-C₂-C₄-alkylenimine.

[0032] The hydrophobically modified poly-C₂-C₄-alkylenimines which are used according to the invention are in part known from the prior art cited at the beginning or can be prepared analogously to the methods described there. As a rule, hydrophobically modified poly-C₂-C₄-alkylenimines are prepared by polymer-analogous reaction of unmodified poly-C₂-C₄-alkylenimines with a hydrophobicizing agent. Accordingly, one embodiment of the invention relates to the use of a hydrophobically modified poly-C₂-C₄-alkylenimine obtainable by a process which comprises the reaction of a nonmodified poly-C₂-C₄-alkylenimine, in particular a nonmodified, branched poly-C₂-C₄-alkylenimine, and specifically a nonmodified, branched polyethylenimine, with a hydrophobicizing agent.

[0033] Examples of suitable hydrophobicizing agents are

[0034] i) long-chain, linear or branched carboxylic acids having 8 to 30 carbon atoms, preferably 10 to 22 carbon atoms, in particular 10 to 18 carbon atoms, in the alkyl or alkenyl radical, such as caprylic acid, pelargonic acid, undecanoic acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, margaric acid, stearic acid, nonadecanoic acid, arachic acid, behenic acid, palmitoleic acid, oleic acid, linoleic acid, linolenic acid, arachidonic acid and mixtures thereof, preferably lauric acid, stearic acid, palmitic acid and oleic acid, or their amide-forming derivatives, such as acid chlorides, esters or anhydrides of the specified carboxylic acids and mixtures thereof,

[0035] ii) linear or branched alkyl halides having 8 to 30 carbon atoms, preferably 10 to 22 carbon atoms, in particular 10 to 18 carbon atoms, in the linear or branched alkyl radical, such as octyl chloride, nonyl chloride, decyl chloride, dodecyl chloride, tetradecyl chloride, hexadecyl chloride, octadecyl chloride and mixtures thereof,

[0036] iii) alkyl epoxides having 8 to 30 carbon atoms, preferably 10 to 22 carbon atoms, in particular 10 to 18 carbon atoms in the linear or branched alkyl radical, such as hexadecenyl oxide, dodecenyl oxide and octadecenyl oxide and mixtures thereof,

[0037] iv) alkyl ketene dimers having 8 to 30 carbon atoms, preferably 10 to 22 carbon atoms, in particular 10 to 18 carbon atoms in the linear or branched alkyl radical, such as lauryl ketene, palmityl ketene, stearyl ketene and oleyl ketene dimers and mixtures thereof,

[0038] v) cyclic dicarboxylic acid anhydrides, in particular alkyl-substituted succinic anhydrides having 8 to 30 car-

bon atoms, preferably 10 to 22 carbon atoms, in particular 10 to 18 carbon atoms, in the linear or branched alkyl radical, such as dodecenylsuccinic anhydride, tetradecylsuccinic anhydride, hexadecenylsuccinic anhydride and mixtures thereof,

[0039] vi) alkyl isocyanates having 8 to 30 carbon atoms, preferably 10 to 22 carbon atoms, in particular 10 to 18 carbon atoms in the linear or branched alkyl radical, such as tetradecyl isocyanate, hexadecyl isocyanate, octadecyl isocyanate and mixtures thereof,

[0040] vii) chloroformic acid esters of linear or branched alkanols or alkenols having 8 to 30 carbon atoms, preferably 10 to 22 carbon atoms, in particular 10 to 18 carbon atoms and mixtures thereof, and

[0041] viii) linear or branched aliphatic aldehydes having 8 to 30 carbon atoms, preferably 10 to 22 carbon atoms, in particular 10 to 18 carbon atoms, and dialkyl ketones having in total 8 to 30 carbon atoms, preferably 10 to 22 carbon atoms, in particular 10 to 18 carbon atoms, in the two alkyl groups and mixtures thereof.

[0042] Preferred hydrophobicizing agents are long-chain, linear or branched carboxylic acids having 8 to 30 carbon atoms, preferably 10 to 22 carbon atoms, in particular 10 to 18 carbon atoms, in the alkyl or alkenyl radical and amide-forming derivatives thereof, in particular linear saturated carboxylic acids having 10 to 22 carbon atoms, in particular 10 to 18 carbon atoms in the alkyl radical.

[0043] Preferred hydrophobicizing agents are also alkyl epoxides having 8 to 30 carbon atoms, preferably 10 to 22 carbon atoms, in particular 10 to 18 carbon atoms.

[0044] The unmodified poly-C₂-C₄-alkylenimines which form the basis of the hydrophobically modified poly-C₂-C₄-alkylenimines used according to the invention comprise homopolymers of ethylenimine (aziridine) and higher homologs thereof, propylenimine (methylaziridine) and butylenimines (1,2-dimethylaziridine, 1,1-dimethylaziridine and 1-ethylaziridine), copolymers of ethylenimine with its higher homologs, and the graft polymers of polyamidoamines or polyvinylamines with ethylenimine and/or its higher homologs.

[0045] Also suitable are the graft polymers of C₂-C₄-alkylenimines described in WO 02/095122, such as ethylenimine onto polyamidoamines or onto polyvinylamines. Such graft polymers generally have a weight fraction of C₂-C₄-alkylenimines of at least 10% by weight, in particular at least 30% by weight, e.g. 10 to 90% by weight in particular 10 to 85% by weight, based on the total weight of the unmodified poly-C₂-C₄-alkylenimine.

[0046] In particular, the unmodified poly-C₂-C₄-alkylenimines are branched poly-C₂-C₄-alkylenimines, preferably polyethylenimines, in particular branched polyethylenimines and specifically homopolymers of ethylenimine, which are in particular branched.

[0047] Preferably, the unmodified poly-C₂-C₄-alkylenimine used for the preparation is branched, where, with regard to the degree of branching, that stated above for hydrophobically modified poly-C₂-C₄-alkylenimines applies.

[0048] Preferably, the unmodified poly-C₂-C₄-alkylenimine used for the preparation has a number-average molecular weight in the range from 1000 to 200 000 Daltons, in particular in the range from 2000 to 100 000 Daltons.

[0049] The reaction of the unmodified poly-C₂-C₄-alkylenimine with the hydrophobicizing agent can take place analo-

gously to known processes in the prior art. The reaction conditions naturally depend on the type and functionality of the hydrophobicizing agent.

[0050] The reaction can take place without a diluent or in solution. The reaction is preferably carried out in a solvent suitable for the reaction. Examples of suitable solvents are hydrocarbons, in particular aromatic hydrocarbons, e.g. alkylbenzenes such as xylenes, toluene, cumene, tert-butylbenzene and the like.

[0051] If appropriate, the reaction can be carried out in the presence of catalysts which improve the reactivity of the hydrophobicizing agent toward the poly-C₂-C₄-alkylenimine. The type of catalyst depends in a manner known per se on the type and reactivity of the hydrophobicizing agent. The catalysts are usually Lewis acids or Brønstedt acids. Often, for example in the case of carboxylic acids, it is possible to dispense with the use of catalysts.

[0052] In the case of the carboxylic acids and carboxylic acid derivatives preferred according to the invention, it has proven advantageous to remove the low molecular weight products (water, alcohols or hydrogen chloride) which form during the reaction from the reaction mixture. For example, in the case of the carboxylic acids, the water formed will preferably be removed from the reaction mixture via an entrainer. Typical entrainers are hydrocarbons, in particular alkyl aromatics such as toluene or xylenes. Preferably, the reaction will then be carried out in an organic solvent suitable as entrainer.

[0053] As a rule, the hydrophobicizing agent will be used in an amount which corresponds to the desired functionality, it also being possible to use the hydrophobicizing agent in excess. In this respect, that stated previously for the functionalization of the hydrophobicized polyalkylenimine applies analogously for the molar ratio of hydrophobicizing agent to nitrogen atoms in the unmodified polyalkylenimine. In particular, the hydrophobicizing agent, calculated as the parts of the hydrophobicizing agent remaining in the product (thus the amount of hydrophobicizing agent minus any low molecular weight products such as water), will be used in an amount of from 0.35 to 20 parts by weight, in particular in an amount of from 0.5 to 10 parts by weight, per part by weight of unmodified poly-C₂-C₄-alkylenimine.

[0054] According to a preferred embodiment of the invention, the hydrophobically modified poly-C₂-C₄-alkylenimines are quaternized. Accordingly, the preparation of the hydrophobically modified poly-C₂-C₄-alkylenimines additionally comprises a quaternization. The quaternization can take place before or in particular after the hydrophobicization.

[0055] For the quaternization, in particular alkylating agents such as alkyl halides which generally have 1 to 10 carbon atoms in the alkyl radical, or dialkyl sulfates, which generally comprise alkyl radicals having 1 to 10 carbon atoms, are used. Examples of suitable alkylating agents from these groups are methyl chloride, methyl bromide, methyl iodide, ethyl chloride, ethyl bromide, propyl chloride, hexyl chloride, dodecyl chloride, lauryl chloride, and dimethyl sulfate and diethyl sulfate. Further suitable alkylating agents are, for example, benzyl halides, in particular benzyl chloride and benzyl bromide; chloroacetic acid; fluorosulfuric acid methyl ester; diazomethane; oxonium compounds, such as trimethylloxonium tetrafluoroborate; alkylene oxides, such as ethylene oxide, propylene oxide and glycidol, which are used in the presence of acids; cationic epichlorohydrins. Preferred quat-

ernizing agents are methyl chloride, dimethyl sulfate and diethyl sulfate. During the quaternization, the secondary or in particular the tertiary nitrogen atoms of the parent poly-C₂-C₄-alkylenimine moiety are converted into quaternary nitrogen atoms, ergo ammonium groups, as a result of which the hydrophobically modified poly-C₂-C₄-alkylenimine is given an overall positive charge.

[0056] The hydrophobically modified poly-C₂-C₄-alkylenimines are generally water-soluble or water-dispersible and can be used in solid and liquid detergents and in laundry aftertreatment compositions. They are characterized in particular by high compatibility with conventional detergent constituents, in particular with the constituents of liquid detergent formulations, specifically those which have a low content of anionic surfactants.

[0057] The incorporation into the respective detergent or laundry aftertreatment composition formulation takes place in a manner known per se, the hydrophobically modified polyalkylenimines often being used in liquid form, i.e. dissolved or dispersed form. The hydrophobically modified polyalkylenimines can also be used in powder or granule form.

[0058] The dye transfer onto fabric washed at the same time and the associated undesired discoloration of this fabric is effectively inhibited. Even at concentrations of from 10 to 150 ppm of the hydrophobically modified poly-C₂-C₄-alkylenimine in the wash or rinse liquor, good to very good dye transfer-inhibiting effects are achieved which lie significantly above the reference substances such as polyvinylpyrrolidone.

[0059] The solid detergent formulations comprise in particular the following components:

[0060] (a) 0.05 to 20% by weight of at least one hydrophobically modified poly-C₂-C₄-alkylenimine,

[0061] (b) 0.5 to 40% by weight of at least one nonionic, anionic and/or cationic surfactant,

[0062] (c) 0.5 to 50% by weight of an inorganic builder,

[0063] (d) 0 to 10% by weight of an organic cobuilder and

[0064] (e) 0.1 to 60% by weight of other customary ingredients, such as extenders, enzymes, perfume, complexing agents, corrosion inhibitors, bleaches, bleach activators, bleach catalysts, further color protection additives and dye transfer inhibitors, graying inhibitors, soil release polyesters, fiber protection additives, silicones, dyes, bactericides and preservatives, dissolution improvers and/or disintegrants, water,

where the sum of components (a) to (e) is 100% by weight.

[0065] The solid detergent formulations may be present in powder, granule, extrudate or tablet form.

[0066] The liquid detergent formulations preferably have the following composition:

[0067] (a) 0.05 to 20% by weight of at least one hydrophobically modified poly-C₂-C₄-alkylenimine,

[0068] (b) 0.5 to 70% by weight of at least one nonionic, anionic and/or cationic surfactant,

[0069] (c) 0 to 20% by weight of an inorganic builder,

[0070] (d) 0 to 10% by weight of an organic cobuilder,

[0071] (e) 0.1 to 60% by weight of other customary ingredients, such as sodium carbonate, enzymes, perfume, complexing agents, corrosion inhibitors, bleaches, bleach activators, bleach catalysts, further color protection additives and dye transfer inhibitors, graying inhibitors, soil release polyesters, fiber protection additives, silicones, dyes, bac-

tericides and preservatives, organic solvents, solubility promoters, hydrotropes, thickeners and/or alkanolamines and

[0072] (f) 0 to 99.35% by weight of water,

where the sum of the components (a) to (f) is 100% by weight.

[0073] The laundry aftertreatment compositions, in particular laundry care rinse compositions, preferably comprise

[0074] (a) 0.05 to 20% by weight of at least one hydrophobically modified poly-C₂-C₄-alkylenimine,

[0075] (b) 0.1 to 40% by weight of at least one cationic surfactant,

[0076] (c) 0 to 30% by weight of at least one nonionic surfactant,

[0077] (d) 0.1 to 30% by weight of other customary ingredients, such as silicones, other lubricants, wetting agents, film-forming polymers, fragrances and dyes, stabilizers, fiber protection additives, further color protection additives and dye transfer inhibitors, complexing agents, viscosity modifiers, soil release additives, solubility promoters, hydrotropes, corrosion protection additives, bactericides and preservatives and

[0078] (e) 0 to 99.75% by weight of water,

where the sum of the components (a) to (e) is 100% by weight.

[0079] Suitable nonionic surfactants (B) here are primarily:

[0080] alkoxylated C₈-C₂₂-alcohols, such as fatty alcohol alkoxylates, oxo alcohol alkoxylates and Guerbet alcohol ethoxylates: the alkoxylation can take place with ethylene oxide, propylene oxide and/or butylene oxide. Block copolymers or random copolymers may be present. Per mole of alcohol, they usually comprise 2 to 50 mol, preferably 3 to 20 mol, of at least one alkylene oxide. A preferred alkylene oxide is ethylene oxide. The alcohols preferably have 10 to 18 carbon atoms;

[0081] alkylphenol alkoxylates, in particular alkylphenol ethoxylates, which comprise C₆-C₁₄-alkyl chains and 5 to 30 mol of alkylene oxide/mol;

[0082] alkyl polyglucosides which comprise C₈-C₂₂-, preferably C₁₀-C₁₈-alkyl chains and as a rule 1 to 20, preferably 1.1 to 5, glucoside units;

[0083] N-alkylglucamides, fatty acid amide alkoxylates, fatty acid alkanolamide alkoxylates, long-chain amine oxides, polyhydroxy(alkoxy) fatty acid derivatives, such as, for example, polyhydroxy fatty acid amides, gemini surfactants, and block copolymers of ethylene oxide, propylene oxide and/or butylene oxide;

and their mixtures.

[0084] Suitable anionic surfactants are, for example:

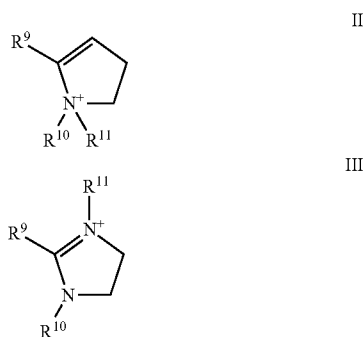
[0085] sulfates of (fatty) alcohols having 8 to 22, preferably 10 to 18, carbon atoms, in particular C₉-C₁₁-alcohol sulfates, C₁₂-C₁₄-alcohol sulfates, C₁₂-C₁₈-alcohol sulfates, lauryl sulfate, cetyl sulfate, myristyl sulfate, palmityl sulfate, stearyl sulfate and tallow fatty alcohol sulfate;

[0086] sulfated alkoxylated C₈-C₂₂-alcohols (alkyl ether sulfates): compounds of this type are prepared, for example, by firstly alkoxyating a C₈-C₂₂-, preferably a C₁₀-C₁₈-alcohol, e.g. a fatty alcohol, and then sulfating the alkoxylation product. For the alkoxylation, ethylene oxide is preferably used;

[0087] linear C₈-C₂₀-alkylbenzenesulfonates (LAS), preferably linear C₉-C₁₃-alkylbenzenesulfonates and alkyltoluenesulfonates;

[0088] alkanesulfonates, in particular C₈-C₂₄-, preferably C₁₀-C₁₈-alkanesulfonates;

- [0089] olefinsulfonates;
 [0090] fatty acid and fatty acid ester sulfonates;
 [0091] soaps, such as the Na and K salts of C₈-C₂₄-carboxylic acids, and mixtures thereof.
 [0092] The anionic surfactants are preferably added to the detergent in the form of salts. Suitable salts here are, for example, alkali metal salts, such as sodium, potassium and lithium salts, and ammonium salts, such as hydroxyethylammonium, di(hydroxyethyl)ammonium and tri(hydroxyethyl)ammonium salts.
 [0093] Particularly suitable cationic surfactants which may be mentioned are:
 [0094] C₇-C₂₅-alkylamines;
 [0095] N,N-dimethyl-N-(hydroxy-C₇-C₂₅-alkyl)ammonium salts;
 [0096] mono- and di(C₇-C₂₅-alkyl)dimethylammonium compounds quaternized with alkylating agents;
 [0097] ester quats, in particular quaternary esterified mono-, di- and trialkanolamines which have been esterified with C₈-C₂₂-carboxylic acids;
 [0098] imidazoline quats, in particular 1-alkylimidazolium salts of the formulae II or III



- [0099] in which the variables have the following meaning:
 [0100] R⁹ is C₁-C₂₅-alkyl or C₂-C₂₅-alkenyl;
 [0101] R¹⁰ is C₁-C₄-alkyl or hydroxy-C₁-C₄-alkyl;
 [0102] R¹¹ is C₁-C₄-alkyl, hydroxy-C₁-C₄-alkyl or a radical R¹-(CO)-X-(CH₂)_m-(X: —O— or —NH—; m: 2 or 3),
 [0103] where at least one radical R⁹ is C₇-C₂₂-alkyl.
 [0104] Suitable amphoteric surfactants are, for example, alkylbetaines, alkylamidobetaines, aminopropionates, aminoglycinates and amphoteric imidazolium compounds.
 [0105] The advantages according to the invention of the hydrophobically modified polyalkylenimines come in useful especially in those detergent formulations which comprise only a small fraction of anionic surfactants. Preferably, the fraction of anionic surfactants, based on the total amount of surfactant in the detergent or laundry aftertreatment composition formulation, is not more than 50% by weight, in particular not more than 30% by weight and specifically not more than 10% by weight. Preferably, the anionic surfactant constitutes not more than 8% by weight, in particular not more than 5% by weight, based on the total weight of the formulation.

- [0106] Suitable inorganic builders are, in particular:
 [0107] crystalline and amorphous aluminosilicates with ion-exchanging properties, such as in particular zeolites: various types of zeolites are suitable, in particular the zeolites A, X, B, P, MAP and HS in their Na form or in forms in which Na is partially replaced by other cations such as Li, K, Ca, Mg or ammonium;
 [0108] crystalline silicates, such as in particular disilicates and sheet silicates, e.g. δ- and β-Na₂Si₂O₅. The silicates can be used in the form of their alkali metal, alkaline earth metal or ammonium salts, preference being given to the Na, Li and Mg silicates;
 [0109] amorphous silicates, such as sodium metasilicate and amorphous disilicate;
 [0110] carbonates and hydrogencarbonates: these can be used in the form of their alkali metal, alkaline earth metal or ammonium salts. Preference is given to Na, Li and Mg carbonates and hydrogencarbonates, in particular sodium carbonate and/or sodium hydrogencarbonate; and
 [0111] polyphosphates, such as pentasodium triphosphate.
 [0112] Suitable organic cobuilders are in particular:
 [0113] low molecular weight carboxylic acids, such as citric acid, hydrophobically modified citric acid, e.g. agaric acid, malic acid, tartaric acid, gluconic acid, glutaric acid, succinic acid, imidodisuccinic acid, oxydisuccinic acid, propanetricarboxylic acid, butanetetracarboxylic acid, cyclopentanetetracarboxylic acid, alkyl- and alkenylsuccinic acids and aminopolycarboxylic acids, e.g. nitrilotriacetic acid, β-alaninediacetic acid, ethylenediaminetetraacetic acid, serinediacetic acid, isoserinediacetic acid, N-(2-hydroxyethyl)iminoacetic acid, ethylenediaminedisuccinic acid and methyl- and ethylglycinediacetic acid or alkali metal salts thereof;
 [0114] oligomeric and polymeric carboxylic acids, such as homopolymers of acrylic acid and aspartic acid, oligomaleic acids, copolymers of maleic acid with acrylic acid, methacrylic acid or C₂-C₂₂-olefins, e.g. isobutene or long-chain α-olefins, vinyl C₁-C₈-alkyl ethers, vinyl acetate, vinyl propionate, (meth)acrylic acid esters of C₁-C₈-alcohols and styrene. Preference is given to the homopolymers of acrylic acid and copolymers of acrylic acid with maleic acid. The oligomeric and polymeric carboxylic acids are used in acid form or as sodium salt;
 [0115] phosphonic acids, such as, for example, 1-hydroxyethylene(1,1-diphosphonic acid), aminotri(methylenephosphonic acid), ethylenediaminetetra(methylenephosphonic acid) and diethylenetriaminopenta(methylenephosphonic acid) and alkali metal salts thereof.
 [0116] Suitable graying inhibitors are, for example, carboxymethylcellulose and graft polymers of vinyl acetate onto polyethylene glycol.
 [0117] Suitable bleaches are, for example, adducts of hydrogen peroxide onto inorganic salts, such as sodium perboratemonohydrate, sodium perboratetetrahydrate and sodium carbonate perhydrate, and percarboxylic acids, such as phthalimidopercaproic acid.
 [0118] Suitable bleach activators are, for example, N,N,N',N'-tetraacetylenethylenediamine (TAED), sodium p-nonanoyloxybenzenesulfonate and N-methylmorpholinium acetoni-trile methyl sulfate.

[0119] Enzymes preferably used in detergents are proteases, lipases, amylases, cellulases, oxidases and peroxidases.

[0120] Suitable further dye transfer inhibitors are, for example, homopolymers, copolymers and graft polymers of 1-vinylpyrrolidone, 1-vinylimidazole or 4-vinylpyridine N-oxide. Homopolymers and copolymers of 4-vinylpyridine reacted with chloroacetic acid are also suitable as dye transfer inhibitors.

[0121] Detergent ingredients are otherwise generally known. Detailed descriptions can be found, for example, in WO-A-99/06524 and 99/04313; in Liquid Detergents, Editor: Kuo-Yann Lai, Surfactant Sci. Ser., Vol. 67, Marcel Dekker, New York, 1997, p. 272-304.

[0122] Application of hydrophobically modified poly-C₂-C₄-alkylenimines according to the invention.

[0123] Selected colored fabric (EMPA 130, EMPA 132, EMPA 133 or EMPA 134) was washed in the presence of white test fabric made of cotton and ballast fabric made of cotton/polyester and also of polyester using a detergent at 60° C. with the addition of the LCST polymers. After the washing cycle, the fabrics were rinsed, spun and dried. In order to determine the dye transfer-inhibiting effect, the coloration of the white test fabric was determined photometrically (Photometer: Elrepho® 2000 from Datacolor). The reflectance values measured at the test fabric were used to determine the color intensity of the coloration in accordance with the method described in A. Kud, Seifen, Öle, Fette, Wachse, volume 119, pages 590-594 (1993). The color intensity for the experiment with the respective test substance, the color intensity for the experiment without test substance and the color intensity of the test fabric before washing were used to ascertain the dye transfer-inhibiting effect of the test substance according to the following formula in %.

$$DTI \text{ effect } [\%] = \frac{\frac{\text{color intensity(without polymer)} - \text{color intensity(with polymer)}}{\text{color intensity(without polymer)}} - \frac{\text{color intensity(before washing)}}{\text{color intensity(before washing)}}}{\text{color intensity(before washing)}} \times 100$$

[0124] The washing conditions are given in Table 1. The composition of detergent A used is given in Table 2. The test results for the dye transfer inhibition are listed in Table 3.

TABLE 1

Washing conditions Washing conditions main wash cycle	
Machine	Laundry-o-meter from Atlas, Chicago, USA
Detergent dosing	5.0 g/l of liquor detergent A
Water hardness	3 mmol/l Ca:Mg 4:1
Liquor ratio	1:16
Wash temperature	60° C.
Wash time	30 min
Polymer dosing	0.05 g/l liquor
Colored fabric	1 g EMPA 130 (C.I. Direct Red 83:1) 1 g EMPA 132 (C.I. Direct Black 22) 1 g EMPA 133 (C.I. Direct Blue 71) 0.5 g EMPA 134 (C.I. Direct Orange 39) (all Swiss Federal Laboratories for Materials Testing, St. Gallen, Switzerland)
Test fabric	5 g cotton fabric 221 (bleached)
Ballast fabric	5 g blended fabric 768 (65:35 polyester:cotton) + 5 g polyester fabric 854

TABLE 2

Composition of detergent A (liquid detergent)	
Ingredients	[% by wt.]
C ₁₃ C ₁₅ -oxo alcohol x 7 EO	12
C ₆ -alcohol x 5 EO	5
Citric acid	3
Propylene glycol	10
Ethanol	2
Diethylenetriaminepenta(methylenephosphonic acid)	1.0
Water	ad 100

[0125] Adjust to pH 9 with sodium hydroxide solution.

Preparation of Hydrophobically Modified Polyethylenimine Derivatives:

Starting Materials:

[0126] Polyethylenimine A: M_w 25 000 g/mol; amine number: 20.14 mmol/g ratio of primary:secondary:tertiary nitrogen atoms: 1.0:1.1:0.7, determined by means of ¹³C-NMR.

[0127] Polyethylenimine B: M_w 5000 g/mol; amine number: 9.22 mmol/g ratio of primary:secondary:tertiary nitrogen atoms: 1.0:1.0:0.7, determined by means of ¹³C-NMR.

Polymer 1

[0128] 350 g of polyethylenimine A were initially introduced into toluene (300 ml). Heating to 100° C. was then carried out. After adding palmitic acid (179 g), the reaction mixture was brought to 120° C. and, while stirring, the water which formed was distilled off via a water separator (7 h). Toluene was then removed under reduced pressure. The product was obtained as an orange, very viscous oil (503 g).

Polymer 2

[0129] 210 g of polyethylenimine A were initially introduced into toluene (300 ml). Heating to 100° C. was then carried out. After adding palmitic acid (322 g), the reaction mixture was brought to 120° C. and, while stirring, the water which formed was distilled off via a water separator (50 h). Toluene was then removed under reduced pressure. The product was obtained as an orange wax (501 g).

Polymer 3

[0130] 200 g of polyethylenimine A were initially introduced into toluene (700 ml). Heating to 100° C. was then carried out. After adding palmitic acid (502 g), the reaction mixture was brought to 120° C. and, while stirring, the water which formed was distilled off via a water separator (30 h). 400 ml of toluene were removed from the reaction mixture and then water was distilled off for a further 12 h. The toluene was then removed under reduced pressure. The product was obtained as a brown wax (670 g).

Polymer 4

[0131] 231 g of polyethylenimine A were initially introduced and heated to 100° C. The C12 epoxide (Vikolox 12; 425 g) was added dropwise. The mixture was then stirred at 100° C. for 9 h. The yellow, highly viscous oil was obtained (656 g).

Polymer 5

[0132] 199 g of polyethylenimine A were initially introduced into toluene (400 ml). Heating to 100° C. was then

carried out. After adding dodecylic acid (396 g), the reaction mixture was brought to 120° C. and, while stirring, the water which formed was distilled off via a water separator (30 h). The toluene was then removed under reduced pressure. A viscous reddish-brown product was obtained (558 g).

Polymer 6

[0133] 149 g of polyethylenimine A were initially introduced into toluene (400 ml) and heated to 100° C. After adding stearic acid (424 g), the reaction mixture was brought to 120° C. and, while stirring, the water which formed was distilled off via a water separator (30 h). The toluene was then removed under reduced pressure. The product was obtained as a yellow-pale brown wax (451 g).

Polymer 7

[0134] 550 g of polyethylenimine B were initially introduced into toluene (500 ml). Heating to 100° C. was then carried out. After adding palmitic acid (258 g), the reaction mixture was brought to 120° C. and, while stirring, the water which formed was distilled off via a water separator (3 d). The toluene was then removed under reduced pressure. The product was obtained as an orange wax (510 g).

Polymer 8

[0135] 434 g of polyethylenimine B were initially introduced into toluene (400 ml). Heating to 100° C. was carried out. After adding palmitic acid (497 g), the reaction mixture was brought to 120° C. and, while stirring, the water which formed was distilled off via a water separator (3 d). The toluene was then removed under reduced pressure. The product was obtained as an orange wax (680 g).

Polymer 9

[0136] Polymer 8 (666 g) was heated to 75° C. Dimethyl sulfate was then metered in (71.8 g; Dosimat 2.5 ml/min). The excess dimethyl sulfate was then removed under reduced pressure. The product was obtained as a brown amorphous substance (407.5 g).

TABLE 3

	Application liquid detergent A			
	DTI effect [%]			
	EMPA 130	EMPA 132	EMPA 133	EMPA 134
Polymer 1	53.6	45.6	70.5	67.1
Polymer 2	84.3	64.7	89.1	83.1
Polymer 3	87.9	68.3	91.4	78.7
Polymer 4	66.1	30.8	80.3	68.0
Polymer 5	86.2	62.7	91.1	84.7
Polymer 6	86.9	72.9	90.9	84.7
Polymer 7	51.8	37.4	72.7	62.5
Polymer 8	85.3	63.5	90.1	75.0
Polymer 9	84.1	67.1	91.4	80.3
PEI 25 000	neg. effect	46.1	40.2	41.7
PEI 5000	neg. effect	54.3	25.8	53.2
PVP*	22.9	33.7	94.0	35.8

PVP = polyvinylpyrrolidone with K value 30

PEI 25 000 = polyethylenimine A

PEI 5000 = polyethylenimine B

Negative effect: polymer does not exhibit inhibition of the dye transfer, but favors it.

*Polyvinylpyrrolidone: reference substance

1. A method for inhibiting dye transfer during washing of textiles with a detergent composition, which comprises at least one hydrophobically modified poly-C₂-C₄-alkylenimines in an amount which is effective for inhibiting dye transfer.

2. The method according to claim 1, where, on average, at least 10 mol % of the nitrogen atoms of the poly-C₂-C₄-alkylenimine carry an aliphatic, saturated or unsaturated hydrocarbon radical which has at least 8 carbon atoms.

3. The method according to claim 2, where the fraction of the hydrocarbon radicals, based on the total weight of the poly-C₂-C₄-alkylenimine, constitutes 25 to 95% by weight.

4. The method according to claim 2, where the hydrocarbon radicals are present in the form of C₈-C₃₀-alkyl-, C₈-C₃₀-alkylcarbonyl-, C₈-C₃₀-alkenyl-, C₈-C₃₀-alkenylcarbonyl-, C₈-C₃₀-alkadienyl-, C₈-C₃₀-alkadienylcarbonyl- and/or hydroxy-C₈-C₃₀-alkyl groups.

5. The method according to claim 1, where the hydrophobically modified poly-C₂-C₄-alkylenimine has a number-average molecular weight in the range from 3000 to 300 000 Daltons.

6. The method according to claim 1, where the hydrophobically modified poly-C₂-C₄-alkylenimine in the poly-C₂-C₄-alkylenimine moiety is branched.

7. The method according to claim 1, where the hydrophobically modified poly-C₂-C₄-alkylenimine has quaternized nitrogen atoms.

8. The method according to claim 1, where the hydrophobically modified poly-C₂-C₄-alkylenimine is obtainable by a process which comprises the reaction of a nonmodified poly-C₂-C₄-alkylenimine with a hydrophobicizing agent.

9. The method according to claim 8, where the hydrophobicizing agent is selected from saturated, mono- or polyunsaturated aliphatic C₉-C₃₁-carboxylic acids, their amide-forming derivatives and C₈-C₃₀-alkylene oxides.

10. The method according to claim 8, where the hydrophobicizing agent, calculated as the parts of the hydrophobicizing agent remaining in the product, is used in an amount of from 0.35 to 20 parts by weight per part by weight of unmodified poly-C₂-C₄-alkylenimine.

11. The method according to claim 8, where the preparation of the hydrophobically modified poly-C₂-C₄-alkylenimine additionally comprises a quaternization.

12. The method according to claim 8, where the unmodified poly-C₂-C₄-alkylenimine used for the preparation is branched.

13. The method according to claim 8, where the unmodified poly-C₂-C₄-alkylenimine used for the preparation has a number-average molecular weight in the range from 1000 to 200 000 Daltons.

14. The method according to claim 1, where the fraction of nonionic surfactants in the detergent composition, based on the total amount of surfactant in the detergent composition, is at least 50% by weight.

15. The method according to claim 1, where the hydrophobically modified poly-C₂-C₄-alkylenimine is used in a concentration of from 5 to 150 ppm in the wash liquor.

16. A method for inhibiting dye transfer during washing of textiles with a detergent composition, which comprises contacting a textile with at least one hydrophobically modified poly-C₂-C₄-alkylenimines in an amount which is effective for inhibiting dye transfer.