REAGENT-MODIFIED PARTICULATE POLYMERS FOR TREATMENT OF THE SURFACE OF TEXTILE AND NON-TEXTILE MATERIALS

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(57) ABSTRACT
A method of treating a surface of a textile or non textile material which comprises applying a reactive modified particulate polymer having a particle size from 10 nm to 100 μm from an aqueous dispersion to the surface of said material and drying said material.
REAGENT-MODIFIED PARTICULATE POLYMERS
FOR TREATMENT OF THE SURFACE OF
TEXTILE AND NON-TEXTILE MATERIALS

[0001] This invention relates to a method for surface treating textile and nontextile materials with reactive modified particulate polymers, the use of the reactive modified particulate polymers, and wrinkleproofing, washing, rinsing, refreshing and textile treatment formulations comprising the reactive modified particulate polymers.

[0002] Cellulosic textiles are given easy care properties by treatment with condensation products of urea, glyoxal and formaldehyde, for example. The finish is applied during the production of textile materials. Softening compounds are frequently further applied with the finish. Thus finished textiles are less wrinkled and creased, easier to iron and softer and smoother after laundering than untreated cellulosics.

[0003] WO 98/04772 discloses a process for pretreating textile materials by applying a mixture of a polyacrylic acid and a cationic softener to the textile materials. Wrinkle control is obtained as a result.


[0005] Washing, rinsing, cleaning and refreshing processes in aqueous media are customarily carried out in a very dilute liquor, and the ingredients of the particular formulation used generally do not remain on the substrate, but are disposed of with the effluent. Sustained modification of the surface of cellulosic materials with dispersed particles in the herebelow mentioned processes is accomplished only to an unsatisfactory degree.

[0006] U.S. Pat. No. 5,476,660 discloses the principle of using polymeric retention aids for cationic or zwitterionic dispersions of polystyrene or wax that contain the active substance embedded in the dispersed particles. These dispersed particles act as carrier particles, since they adhere to the treated surface where they release an active substance, for example in the case of use in surfactant formulations.

[0007] U.S. Pat. No. 3,993,830 discloses applying a non-permanent soil-release finish to a textile material by treating the textile material with a dilute aqueous solution comprising a polyacrylate and a water-soluble salt of polyvalent metal. Preferred polyacrylates are said to be water-soluble copolymers of ethylenically unsaturated monomeric acids and alkyl acrylates. The mixtures are released in the rinse cycle of a home laundry process.

[0008] It is an object of the present invention to provide a further method for modifying surfaces of textile and non-textile materials.

[0009] More particularly, it is an object of the present invention to provide a method for wrinkleproofing cellulosic textiles.

[0010] It is a further object of the present invention to provide a method for improving the soil release from textiles and non-textile surfaces.

[0011] We have found that this object is achieved in this invention by a method of treating a textile material, which comprises applying a reactive modified particulate polymer having a particle size from 10 nm to 100 \( \mu \)m from an aqueous dispersion to the surface of the textile material and drying the textile material.

[0012] The invention further provides for the use of the reactive modified particulate polymers as surface-modifying ingredient in rinsing, refreshing or washing compositions and also laundry detergent, refreshing and textile treatment formulations comprising the particulate polymers.

[0013] Reactive modified polymers for the purposes of the invention are particulate polymers containing reactive, crosslinking groups. The reactive modified polymers may contain units derived from anionic and/or cationic monomers and may have anionic, cationic or amphoteric protective colloids or emulsifiers at their surface. The reactive modified polymers may contain units derived from monomers containing reactive groups and/or may have at their surface protective colloids or emulsifiers that contain reactive groups. Reactive modified polymers of anionic character, i.e., which contain anionic groups and/or are dispersed using anionic protective colloids or emulsifiers, may have a coating with cationic polymers at their surface.

[0014] The reactive groups may also have a postcrosslinking effect, i.e., develop their crosslinking effect only on heating or drying of the treated textile surfaces.

[0015] The reactive modified particulate polymers are obtainable by copolymerization of ethylenically unsaturated monomers containing no crosslinking reactive groups with ethylenically unsaturated monomers which do contain such crosslinking reactive groups. But the reactive groups may also be introduced into the polymer by coating the surfaces of the polymer particles with colloids having crosslinking reactive groups.

[0016] The reactive modified polymers used according to the invention are in one embodiment of the invention obtainable by copolymerizing ethylenically unsaturated monomers containing no reactive groups with ethylenically unsaturated monomers containing reactive groups.

[0017] Useful monomers containing no reactive groups include for example alkyl esters of \( C_1-C_5 \) monoethylenically unsaturated carboxylic acids with monohydric \( C_3-C_{22} \) alcohols, hydroxyalkyl esters of \( C_3-C_5 \) monoethylenically unsaturated carboxylic acids with dihydric \( C_2-C_4 \) alcohols, vinyl esters of saturated \( C_1-C_{15} \) carboxylic acids, ethylene, propylene, isobutylene, \( C_4-C_{12} \) alpha-olefins, butadiene, styrene, alpha-methylstyrene, acrylonitrile, methacrylonitrile, tetrafluoroethylene, vinylidene fluoride, fluoroethylene, chlorotrifluoroethylene, hexafluoropropene or mixtures thereof.

[0018] Preferred monomers are methyl acrylate, ethyl acrylate, n-butyl acrylate, sec-butyl acrylate, tert-butyl acrylate, ethylhexyl acrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, methyl methacrylate, n-butyl methacrylate, vinyl acetate, vinyl propionate, styrene, ethylene, propylene, butylene, isobutene, diisobutene and tetrafluoroethylene, and particularly preferred monomers are methyl acrylate, ethyl acrylate, n-butyl acrylate, styrene, methacrylate and vinyl acetate.

[0019] Useful reactive, crosslinking groups include for example azetidinium, glycylid ether, halohydrin, carboxylic
anhydride, carbonyl chloride, isocyanate, vinyl sulfone, N-methyl, aldehyde and imine groups.

[0020] Preferred unsaturated monomers containing reactive groups are N-methyl(methyl)acrylamide, glycidyl methacrylate, methacryloyloxypropyltrimethylsilyl, vinyltrimethoxysilane, m-isoproponylbenzyl isocyanate, acrolein, isobutoxymethacrylamide, isobutotmethacrylamide, hydroxyethylated diacetoneacrylamide, allyl N-methyldicarbamate, N-formyl-N-acryloyloxyethylendiamine, gamma-methylacryloyloxypropyltrimethoxysilane, methacryloyloxyethyltrimethysilane, epithiopropyl methacrylate, vinyl chloride, 2-chloroethyl acrylate, 4-chlorobutyl acrylate, 3-chloro-2-hydroxypropyl acrylate, methyl 1-(chloromethyl)acrylate, 2-(bromomethyl)acrylonitrile, 2-(chloromethyl)acrylamide, 6-bromo-2-naphthylacrylate, 2-(4-chloro-2-nitrovinyl)ethyl acrylate, 6-chloro-5-(trichloromethyl)-2-norbornyl acrylate, 3-chloro-2-{[dimethylphosphinyl]oxy}propyl acrylate, 3-chloro-2-{[(1-oxo-3-phenyl-2-propenyl)oxy]propyl methacrylate, 2-phenylallyl bromide, p-chloromethylstyrene, vinyl monochloroacetate, 2-(4-ethoxyphenyl)-25-oxazolinyl methacrylate.

[0021] The reactive modified polymers used according to the invention may be prepared by the conventional methods of solution, precipitation, suspension or emulsion polymerization described for example in P. Lovell and M. S. El-Aasser, Emulsion Polymerisation and Emulsion Polymers, Wiley, New York, 1997. Preferably, the reactive modified particulate polymers used according to the invention are obtained by emulsion polymerization in an aqueous medium.

[0022] The polymerization is conducted in the presence of polymerization initiators that decompose either thermally or photochemically or in the presence of redox initiators. Of the polymerization initiators that decompose thermally, preference is given to those which decompose in the range from 20 to 180°C, especially from 50 to 90°C.

[0023] Preferred polymerization initiators for the emulsion polymerization are water-soluble organic peroxides such as peresters, percarbonates, perketals, hydroperoxides, inorganic peroxides such as H₂O₂, salts of peroxydisulfuric acid and peroxodisulfuric acid, azo compounds, boron-alkyl compounds and also hydrocarbons that decompose homolytically.

[0024] The polymerization initiators, which are used in amounts in the range from 0.01 to 15% by weight, based on the monomers, can be used individually or in combination.

[0025] An emulsion polymerization to prepare the polymers is generally carried out by using dispersing assistants.

[0026] Useful dispersing assistants include water-soluble macromolecular organic compounds having polar groups, such as polyvinylpyrrolidone, copolymers of vinyl propionate or acetylene and vinylpyrrolidone, partially hydrolyzed copolymers of an acrylic ester, and acrylonitrile, polyvinyl alcohols having different residual acetate contents, cellulose ethers, gelatin, block copolymers, modified starch, low molecular weight carboxyl- and/or sulf-containing polymers or mixtures thereof. Useful natural protective colloids include water-soluble proteins, partially degraded proteins, water-soluble cellulose ethers, native starches, degraded starches and/or chemically modified starches. Examples of water-soluble cellulose esters are hydroxyethylcellulose and methylcellulose. Useful natural starches include those obtainable by heating in an aqueous medium to above the gelatinization temperature. It is also possible to use degraded starches that are obtainable by hydrolytic, oxidative or enzymatic degradation.

[0027] Particularly preferred protective colloids are polyvinyl alcohols having a residual acetate content from 0 to 39%, especially from 5 to 39%, mol % and vinylpyrrolidone/vinyl propionate copolymers having a vinyl ester content of up to 35%, especially from 5 to 30%, by weight.

[0028] Useful dispersing assistants further include nonionic or ionic emulsifiers and also mixtures thereof. Preferred emulsifiers are optionally ethoxylated or propoxylated long-chain alkanols or alkylphenols having different degrees of ethoxylation or propanolysis, for example adducts with from 0 to 50 mol of alkylene oxide, and their neutralized, sulfonated or phosphated derivatives. Neutralized dialkyl sulfosuccinates or alkyl diphenyl oxide disulfonates are particularly useful.

[0029] Useful dispersing assistants further include cationic emulsifiers based on C₅-C₉ alkylamines, N,N-dimethyl-N(C₅-C₆-hydroxyalkyl)amonium salts, mono- and dio-(C₅-C₉-alkyldimethylammonium) compounds quaternized with alkylation agents, estrer quats, such as quaternary esterified mono-, di- or trialkolamines esterified with C₅-C₉ carboxylic acids, and amidazoline quats, such as 1-alkylimidazolinium salts.

[0030] The polymers have for example molar masses from 1000 to 2 million, preferably from 5000 to 500000, and usually the molar masses of the polymers are in the range from 10000 to 150000.

[0031] The molar masses of the polymers can be limited by using customary regulators in the polymerization. Examples of typical regulators are mercapto compounds such as mercaptotetanol or thioglycolic acid.

[0032] To increase the density of the reactive groups at the surface of the polymer particles, the monomers containing reactive groups can be added in stages and separately from the other monomers. Preferably, the predominant portion of the monomers containing reactive groups is not added until toward the end of the total feed time for all monomers. In a variant for preparing the polymers used according to the invention, 70% of the monomers containing the reactive groups are added in the last third of the total feed time.

[0033] As well as the polymerization methods mentioned, other methods may also be used for preparing the particular polymers used according to the invention. For instance, particulate polymers can be precipitated by lowering the solubility of dissolved polymers a solvent. For example, a polymer containing an acidic group can be dissolved in a suitable, water-miscible solvent and the solution metered into an excess of water in such a way that the pH of the initial charge is at least 1 lower than the equivalent pH of the copolymer. By equivalent pH is meant that pH at which 50% of the acidic groups of the copolymer are neutralized. This method may require the use of a dispersing assistant, pH regulators and/or salts in order that stable, finely divided aqueous dispersions may be obtained.

[0034] The reactive modified polymers used in the invention have a particle size from 10 nm to 100 μm, preferably from 30 nm to 3 μm, especially from 50 nm to 800 nm.
The reactive modified polymers used according to the invention may be of anionic, cationic, amphoteric or nonionic character.

Reactive modified polymers of anionic character are obtainable by copolymerizing anionic monomers such as acrylic acid, methacrylic acid, styrenesulfonic acid, acrylicamid-2-methylpropanesulfonic acid, vinylsulfonic acid and maleic acid, monomalesates with \( C_1-C_6 \) alkanols and/or salts thereof, which may be done in the presence of emulsifiers and protective colloids. Anionic monomers as the term is used herein also comprehends monomers having acidic groups which are convertible into their salts, even though these are not present in ionic form during the polymerization.

The anionic character for the polymers is also obtainable by conducting the copolymerization in the presence of anionic protective colloids and/or anionic emulsifiers.

But the anionic character for the polymers may also be obtained by emulsifying or dispersing the finished polymers in the presence of anionic protective colloids and/or anionic emulsifiers.

Reactive modified polymers of cationic character are obtainable by including cationic monomers in the copolymerization, which may be carried out in the presence of emulsifiers and protective colloids. Cationic monomers are herein also to be understood as meaning monomers having basic groups which are convertible into their salts, even though these are not present in ionic form during the polymerization. Useful cationic monomers include nitrogenous basic ethylenically unsaturated monomers in the form of the free bases, the salts with organic or inorganic acids or in quaternized form. Useful nitrogenous basic ethylenically unsaturated compounds include for example \( N,N \)-dialkylaminomethyl (meth)acrylates, for example dimethylaminomethyl acrylate, dimethylaminoethyl methacrylate, diethyl aminoethyl acrylate, diethylaminoethyl methacrylate, dimethylaminopropyl acrylate, dimethylaminoethyl methacrylate, diethylaminomethyl propyl acrylate, diethylaminomethyl methacrylate, dimethylaminobutyl acrylate, dimethylaminobutyl methacrylate, dimethylaminopropyl acrylate, dimethylaminopropyl methacrylate, dimethylaminobutyraldehyde. Useful basic monomers of this group further include \( N,N \)-dialkylaminomethyl (meth)acrylamides, for example \( N,N \)-di-\( C_1-C_6 \)-alkylamino-\( C_2-C_4 \)-alkyl(meth)acrylamides, such as dimethylaminooethylacrylamide, dimethylaminomethacrylamide, diethylaminomethylacrylamide, diethylaminoethylmethacrylamide, dipropylaminomethylacrylamide, dipropylaminomethacrylamide, dimethylaminopropylacrylamide, dimethylaminopropylmethacrylamide, dimethylaminobutylacrylamide, dimethylaminobutylmethacrylamide and dimethylaminobutylacrylamide.

Useful monomers of this group further include 4-vinylpyridine, 2-vinylpyridine, 2-vinylimidazole, 2-methyl-1-vinylimidazole and/or diallyl(di)alkylamines where the alkyl group contains from 1 to 12 carbon atoms. The abovementioned basic monomers are used in the copolymerization in the form of the free bases, the salts with organic or inorganic acids or in quaternized form. Useful carboxylic acids for salt formation include for example carboxylic acids containing from 1 to 7 carbon atoms, for example formic acid, acetic acid or propionic acid, benzenecarboxylic acid, sulfuric acid, phosphoric acid, \( C_3 \)-toluenesulfonic acid or inorganic acids such as halohydrin acids, for example hydrochloric acid or bromohydrinic acid. The basic monomers mentioned above by way of illustration may also be used in quaterminated form. Useful quaternizing agents include for example alkyl halides having from 1 to 18 carbon atoms in the alkyl group, for example methyl chloride, methyl bromide, methyl iodide, ethyl chloride, propyl chloride, hexyl chloride, dodecyl chloride, lauryl chloride and benzyl halides, especially benzyl chloride and benzyl bromide. The nitrogenous basic monomers may also be quaternized by reacting these compounds with dialkyl sulfates, especially diethyl sulfate or dimethyl sulfate. Examples of quaternized monomers of this group are trimethylammonium methyl methacrylate chloride, dimethylthylammoniumethyl methacrylate ethyl sulfate and dimethylethylammonium methylmethacrylamide ethyl sulfate, 3-methyl-1-vinylimidazolium chloride.

But the cationic character for the polymers is also obtainable by conducting the copolymerization in the presence of cationic protective colloids and/or cationic emulsifiers.

But the cationic character for the polymers mentioned is also obtainable by emulsifying or dispersing the finished polymers in the presence of cationic protective colloids and/or cationic emulsifiers.


Reactive modified polymers of amphoteric character are obtainable by including both cationic and anionic monomers. Useful monomers include for example the aforementioned cationic and anionic monomers.

The amphoter character for the polymers is also obtainable by conducting the copolymerization in the presence of amphoteric protective colloids and/or amphoter emulsifiers.

But the amphoter character for the polymers is also obtainable by emulsifying or dispersing the finished polymers in the presence of amphoteric protective colloids and/or amphoter emulsifiers.

Reactive modified polymers are obtainable for example by copolymerization of

(a) from 40 to 99.9% by weight, preferably from 50 to 90% by weight, particularly preferably from 60 to 75% by weight, of at least one sparingly water-soluble or water-insoluble nonionic monomer,

(b) from 0 to 60% by weight, preferably from 1 to 55% by weight, particularly preferably from 5 to 30% by weight, especially from 15 to 40% by weight, of carboxyl-containing monomers or salts thereof,

(c) from 0 to 25% by weight, preferably from 0 to 15% by weight, of sulfon- and/or phosphon-containing monomers or salts thereof,

(d) from 0 to 30% by weight, preferably from 0 to 15% by weight, of cationic monomers,
(0052) (e) from 0 to 55% by weight, preferably from 0 to 40% by weight, of water-soluble nonionic monomers;

(0053) (f) from 0 to 30% by weight, preferably from 0 to 10% by weight, of multiply ethylenically unsaturated monomers, and

(0054) (g) from 0.1 to 30% by weight, preferably from 0.25 to 15% by weight, particularly preferably from 0.5 to 10% by weight, of at least one ethylenically unsaturated monomer containing reactive, crosslinking groups.

(0055) Polymers containing units derived from at least one anionic monomer b) or c) can be used without additional anionic emulsifiers or protective colloids. Polymers containing less than 0.5% by weight of units derived from anionic monomers are usually used together with at least one anionic emulsifier or protective colloid.

(0056) Preferred monomers a) are methyl acrylate, ethyl acrylate, n-butyl acrylate, sec-butyl acrylate, tert-butyl acrylate, ethylhexyl acrylate, hydroxethyl acrylate, hydroxypropyl acrylate, methyl methacrylate, n-butyl methacrylate, vinyl acetate, vinyl propionate, styrene, ethylene, propylene, butylene, isobutene and tetrafluoroethylene, and particularly preferred monomers are methyl acrylate, ethyl acrylate, n-butyl acrylate, styrene, methyl methacrylate and vinyl acetate.

(0057) Preferred monomers b) are acrylic acid, methacrylic acid, maleic acid or monomaleates with C1-C18 alkanols.

(0058) Useful monomers c) include for example acrylicsido-2-methylpropanesulfonic acid, vinylsulfonic acid, methallylsulfonic acid and also their alcali metal and ammonium salts.

(0059) Useful monomers d) include for example dimethylaminomethyl methacrylate, dimethylaminopropylacrylamide, 1-vinylimidazole, 3-methyl-1-vinylimidazolinium chloride and 4-vinylpyridine.

(0060) Useful monomers e) include for example acrylamide, methacrylamide, N-vinylformamide, N-vinylacetamide, N-vinylpyrrolidone, N-vinylloxazolidone, methyl polyglycol acrylates, methyl polyglycol methacrylates, methylpolyglycolacrylamides and vinylcaprolactam.

(0061) Useful polyunsaturated monomers f) include for example acrylic esters, methacrylic esters, allyl ethers and vinyl ethers of at least dihydric alcohols. The OH groups of the underlying alcohols may be wholly or partly etherified or esterified. Crosslinkers contain at least two ethylenically unsaturated groups. Examples are butanedioic diacrylate, hexanedioic diacrylate and trimethylpropane triacrylate. Useful unsaturated monomers e) further include for example allyl esters of unsaturated carboxylic acids, divinylibenzene, methylenebisacrylamide and divinylurea.

(0062) Preferred crosslinking but mainly postcrosslinking unsaturated monomers g) containing reactive groups are N-methyl(meth)acrylamide, glycidyl methacrylate, methacryloyloxypropyltrimethoxysilane, vinyltrimethoxysilane, m-isopropenylbenzoyl isocyanate, acrolein, isobutoxymethylacrylamide, hydroxymethylated diacetoneacrylamide, allyl N-methylolcarbamate, N-formyl-N-acryloyloxymethylenediamine, gamma-methylacryloyloxypropyltrimethoxysilane, methacryloyloxyethoxytrimethylsilane, epichlorohydrin methacrylate, vinyl chloride, 2-chloroethyl acrylate, 4-chlorobutyl acrylate, 3-chloro-2-hydroxypropyl acrylate, methyl 1-(chloromethyl)acrylate, 2-(bromomethyl)acrylonitrile, 2-(chloromethyl)acrylamide, 6-bromo-2-naphthylacrylate, 2-(4-chloro-2-nitroanilino)ethyl acrylate, 6-chloro-5-(trichloromethyl)-2-norbomyl acrylate, 3-chloro-2-(dimethylphosphonylethoxy)propyl acrylate, 3-chloro-2-(1-oxo-3-phenyl-2-propenyl)oxypropyl methacrylate, 2-phenylallyl bromide, p-chloromethylstyrene, vinyl monochloroacetate, 2-(4-ethoxyphenyl)-2-oxazolinyl methacrylate.

(0063) One embodiment of the invention comprises using reactive modified particulate polymers having an anionic character, i.e., containing anionic groups and/or being dispersed with anionic protective colloids or emulsifiers and having a coating of cationic polymer on their surface.

(0064) These reactive modified particulate polymers which have been catenionically modified are obtainable by coating the surface of the anionically dispersed, particulate polymers with cationic polymers. Useful cationic polymers include all natural or synthetic cationic polymers which contain amino and/or ammonium groups and are water soluble. Examples of such cationic polymers are polymers containing vinylamine units, polymers containing vinylimidazole units, polymers containing quaternary vinylimidazole units, condensates of imidazole and epichlorohydrin, crosslinked polyamidoamines, ethyleneimine-grafted crosslinked polyamidoamines, polymethyleneimines, alkoxylated polyethyleneimines, crosslinked polyethyleneimines, amidated polyethyleneimines, alkylated polyethyleneimines, polyamines, amine-epichlorohydrin polycondensates, alkoxylated polyamines, polyallylamines, polydimethylallylammonium chloride, polymers containing basic (methyl)acrylamide or methacrylate units, polymers containing basic quaternary (methyl)acrylamide or methacrylate units and/or lysine condensates.

(0065) Cationic polymers also include amphoteric polymers having a net cationic charge, i.e., the polymers contain anionic as well as cationic monomers in copolymerized form, but the molar fraction of the cationic units present in the polymer is larger than that of the anionic units.

(0066) Polymers containing vinylamine units are prepared for example from open-chain N-vinylcarboxamides of the formula (I)

\[
\begin{align*}
\text{CH}_2\text{CH} & \text{CH} \quad \text{N} \quad \text{R}^1 \\
\text{O} & \quad \text{R}^2
\end{align*}
\]

where R1 and R2, which may be identical or different, are each selected from the group consisting of hydrogen and C1-C4-alkyl. Useful monomers include for example N-vinylformamide (R=H in formula I), N-vinyl-N-methylformamide, N-vinylacetamide, N-vinyl-N-methylacetamide, N-vinyl-N-ethylacetamide, N-vinyl-N-
methylpropionamide and N-vinylpropionamide. The monomers mentioned may be polymerized either alone or mixed with each other or together with other monoethylenically unsaturated monomers to prepare the polymers. Preference is given to starting from homo- or copolymers of N-vinylformamide. Polymers containing vinylamine units are known for example from U.S. Pat. No. 4,421,602, EP-A-0 216 387 and EP-A-0 251 182. They are obtained by hydrolysis, with acids, bases or enzymes, of polymers containing monomers of the formula I in polymerized form.

[0068] Useful monoethylenically unsaturated monomers for copolymerization with N-vinylcarboxamides include all compounds that are copolymerizable therewith. Examples thereof are vinyl esters of saturated carboxylic acids of from 1 to 6 carbon atoms such as vinyl formate, vinyl acetate, vinyl propionate and vinyl butyrate and vinyl ethers such as C₂-C₃-alkyl vinyl ethers, for example methyl vinyl ether or ethyl vinyl ether. Useful comonomers further include ethylenically unsaturated C₂-C₆-carboxylic acids, for example acryl acid, methacryl acid, maleic acid, crotonic acid and vinylactic acid and also their alka lmetal and alkaline earth metal salts, esters, amides and nitriles of the carboxylic acids mentioned, for example methyl acrylate, methyl methacrylate, ethyl acrylate and ethyl methacrylate.

[0069] Useful monoethylenically unsaturated monomers for copolymerization with N-vinylcarboxamides further include carboxylic esters derived from glycols or polyalkylene glycols where in each case only one OH group is esterified, for example hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate and also monoacrylate esters of polyalkylene glycols having a molar mass from 500 to 10000.

[0070] Useful comonomers further include esters of ethylenically unsaturated carboxylic acids with amino alcohols such as dimethyleniminoacrylic acid, dimethyleniminoethyl methacrylate, diethylmethyleneimino acrylate, diethylmethyleneiminoethyl methacrylate, dimethylaminopropyl acrylate, dimethylaminopropyl methacrylate, diethylaminopropyl acrylate, dimethylaminobutyl acrylate and diethylaminobutyl acrylate. Basic acrylates can be used in the form of the free bases, the salts with mineral acids such as hydrochloric acid, sulfuric acid or nitric acid, the salts with organic acids such as formic acid, acetic acid, propionic acid or sulfonic acids or in quaternized form. Useful quaternizing agents include for example dimethyl sulfate, diethyl sulfate, methyl chloride, ethyl chloride or benzyl chloride.

[0071] Useful comonomers further include amides of ethylenically unsaturated carboxylic acids such as acrylamide, methacrylamide and also N-alkylaminoamides and -diamides of monoethylenically unsaturated carboxylic acids with alkyl radicals of from 1 to 6 carbon atoms, for example N-methylacrylamide, N,N-dimethylacrylamide, N-methylmethacrylamide, N-ethylacrylamide, N-propylacrylamide and tert-butylacrylamide and also basic (meth)acylamides, for example dimethylaminooethylacrylamide, dimethylaminoethylmethacrylamide, diethylaminooethylacrylamide, diethylaminooethylmethacrylamide, dimethylaminopropylacrylamide, diethylaminopropylacrylamide, dimethylaminopropylmethacrylamide and diethylaminopropylmethacrylamide.

[0072] Useful comonomers further include N-vinylpyrrolidone, N-vinylcaprolactam, acrylonitrile, methacrylonitrile, N-vinylimidazolone and also substituted N-vinylimidazoles such as, for example N-vinyl-2-methylimidazole, N-vinyl-4-methylimidazole, N-vinyl-5-methylimidazole, N-vinyl-2-ethylimidazole and N-vinylimidazolines such as N-vinylimidazolone, N-vinyl-2-methylimidazolone and N-vinyl-2-ethylimidazolone. N-Vinylimidazoles and N-vinylimidazolines are used not only in the form of their free bases but also after neutralization with mineral acids or organic acids or after quaternization, a quaternization being preferably effected with dimethyl sulfate, diethyl sulfate, methyl chloride or benzyl chloride. Also useful are diallyldialkylammonium halides, for example diallyldimethylammonium chlorides.

[0073] Useful comonomers further include sulfo-containing monomers, for example vinylsulfonic acid, allylsulfonic acid, methallylsulfonic acid, styrenesulfonic acid, the alkali metal or ammonium salts of these acids or 3-sulfopropyl acrylate, and the amphoteric copolymers contain more cationic units than anionic units, so that there has a net cationic charge.

[0074] The copolymers contain for example

[0075] from 99.99 to 1 mol %, preferably from 99.9 to 5 mol %, of N-vinylcarboxamides of the formula I and

[0076] from 0.01 to 99 mol %, preferably from 0.1 to 95 mol %, of other monoethylenically unsaturated monomers copolymerizable therewith

[0077] in copolymerized form.

[0078] To prepare polymers containing vinylamine units, it is preferable to start from homopolymers of N-vinylformamidine or from copolymers obtainable by copolymerization of

[0079] N-vinylformamidine with

[0080] vinyl formate, vinyl acetate, vinyl propionate, acrylonitrile, N-vinylcaprolactam, N-vinylurea, acrylic acid, N-vinylpyrrolidone or C₂-C₃-alkyl vinyl ethers

[0081] and subsequent hydrolysis of the homo- or copolymers to form vinylamine units from the copolymerized N-vinylformamidine units, the degree of hydrolysis being for example in the range from 0.1 to 100 mol %.

[0082] The hydrolysis of the hereinabove described polymers is effected according to known processes by the action of acids, bases or enzymes. This converts the copolymerized monomers of the hereinabove indicated formula I through detachment of the group

\[ \text{C} - \text{R}^2 \]

where \( \text{R}^2 \) is as defined for the formula I, into polymers which contain vinylamine units of the formula (III)
where $R^1$ is as defined for the formula I. When acids are used as hydrolyzing agents, the units III are present as ammonium salt.

The homopolymers of the N-vinylcarboxamides of the formula I and their copolymers may be hydrolyzed to an extent in the range from 0.1 to 100 mol %, preferably to an extent in the range from 70 to 100 mol %. In most cases, the degree of hydrolysis of the homo- and copolymers is in the range from 5 to 55 mol %. The degree of hydrolysis of the homopolymers is synonymous with the vinylamine units content of the polymers. In the case of copolymers containing units derived from vinyl esters, the hydrolysis of the N-vinylformamide units can be accompanied by a hydrolysis of the ester groups with the formation of vinyl alcohol units. This is the case especially when the hydrolysis of the copolymers is carried out in the presence of aqueous sodium hydroxide solution. Copolymerized acrylonitrile is likewise chemically modified in the hydrolysis, for example converted into amide groups or carboxyl groups. The homo- and copolymers containing vinylamine units may optionally contain up to 20 mol % of amide units, formed for example by reaction of formic acid with two adjacent amino groups or by intramolecular reaction of an amino group with an adjacent amide group, for example of copolymerized N-vinylformamide. The molar masses of the polymers containing vinylamine units range for example from 1000 to 10 million, preferably from 10000 to 5 million (determined by light scattering). This molar mass range corresponds for example to $K$ values of from 5 to 300, preferably from 10 to 250 (determined by the method of H. Fikentscher in 5% aqueous sodium chloride solution at 25°C and a polymer concentration of 0.5% by weight).

The polymers containing vinylamine units are preferably used in salt-free form. Salt-free aqueous solutions of polymers containing vinylamine units are preparable for example from the hereinabove described salt-containing polymer solutions by ultrafiltration using suitable membranes having molecular weight cutoffs at for example from 1000 to 50000 dalton, preferably from 10000 to 30000 dalton. The hereinbelow described aqueous solutions of other polymers containing amino and/or ammonium groups are likewise obtainable in salt-free form by ultrafiltration.

Useful cationic polymers further include polyethyleneimines. Polyethyleneimines are prepared for example by polymerizing ethylenimine in aqueous solution in the presence of acid-detaching compounds, acids or Lewis acids. Polyethyleneimines have for example molar masses of up to 2 million, preferably from 200 to 500000. Particular preference is given to using polyethyleneimines having molar masses of from 500 to 100000. Useful polyethyleneimines further include water-soluble crosslinked polyethyleneimines which are obtainable by reaction of polyethyleneimines with crosslinkers such as epichlorohydrin or bischlorohydrin ethers of polyalkylene glycols containing from 2 to 100 ethylene oxide and/or propylene oxide units.

Also useful are amidic polyethyleneimines which are obtainable for example by amidation of polyethyleneimines with C$_2$-C$_{12}$-monocarboxylic acids. Useful cationic polymers further include allylated polyethyleneimines and alkoxylated polyethyleneimines. Alkoxylation is carried out using for example from 1 to 5 ethylene oxide or propylene oxide units per NH unit in the polyethyleneimine.

Useful polymers containing amino and/or ammonium groups also include polyamidoamines, which are preparable for example by condensing dicarboxylic acids with polyamines. Useful polyamidoamines are obtained for example when dicarboxylic acids having from 4 to 10 carbon atoms are reacted with polylkylenepolyamines containing from 3 to 10 basic nitrogen atoms in the molecule. Useful dicarboxylic acids include for example succinic acid, malic acid, adipic acid, glutaric acid, suberic acid, sebacic acid or terephthalic acid. Polyamidoamines may also be prepared using mixtures of dicarboxylic acids as well as a mixture of plural polylkylenepolyamines. Useful polylkylenepolyamines include for example diethylenetriamine, triethylenetetramine, tetraethylenepentamine, dipropylenetriamine, tripropylenetetramine, dibexamethylenetetramine, aminopropylenediamine and bis-aminopropyleneethylene diamine. The dicarboxylic acids and polylkylenepolyamines are heated at an elevated temperature, for example at from 120 to 220°C, preferably at from 130 to 180°C, to prepare the polyamidoamines. The water of condensation formed is removed from the system. The condensation may also employ lactones or lactams of carboxylic acids having from 4 to 8 carbon atoms. The amount of a polylkylenepolyamine used per mole of a dicarboxylic acid is for example in the range from 0.8 to 1.4 mol.

Amino-containing polymers further include ethyleneimine-grafted polyamidoamines. They are obtainable from the hereinabove described polyamidoamines by reaction with ethylenimine in the presence of acids or Lewis acids such as sulfuric acid or boron trifluoride ethers at for example from 80 to 100°C. Compounds of this kind are described for example in DE-B-24 34 816.

Useful cationic polymers also include crosslinked or uncrosslinked polyamidoamines which may additionally have been grafted with ethylenimine prior to crosslinking. Crosslinked ethylenimine-grafted polyamidoamines are water soluble and have for example an average molar weight of from 3000 to 1 million dalton. Customary crosslinkers include for example epichlorohydrin or bischlorohydrin ethers of alkylene glycols and polylkylene glycols.

Further examples of cationic polymers that contain amino and/or ammonium groups are polyallyldimethylammonium chlorides. Polymers of this kind are likewise known.

Useful cationic polymers further include copolymers of for example 1-99 mol %, preferably 30-70 mol %, of acrylamide and/or methacrylamide and 99-1 mol %, preferably 70-30 mol %, of cationic monomers such as dialkylaminoalkylacrylamide, dialkylaminoalkylacrylate, dialkylaminoalkylmethacrylamide and/or dialkylaminoalkyl methacrylate. The basic acrylamides and methacrylamides are preferably likewise present in acid-neutralized form or in quaternized form. Examples are N-trimethylammoniumethylacrylamide chloride, N-trimethylammoniummethylmethacrylamide chloride, N-trimethylammoniummethylacrylamide chloride, N-trimethylammoniummethylmethacrylamide chloride.
methacrylate chloride, N-trimethylammonium methyl acrylate chloride, trimethylammonium methacrylamide methosulfate, trimethylammoniummethylmethacrylamide methosulfate, N-ethyltrimethylammoniummethylacrylamide ethosulfate, N-ethyltrimethylammoniummethylmethacrylamide ethosulfate, trimethylammoniumpropylacrylamide chloride, trimethylammoniumpropylmethacrylamide chloride, trimethylammoniumpropylacrylamide methosulfate, trimethylammoniumpropylmethacrylamide methosulfate and N-ethyltrimethylammoniumpropylacrylamide ethosulfate. Preference is given to trimethylammoniumpropylmethacrylamide chloride.

[0093] Further useful cationic monomers for preparing (meth)acrylamide polymers are diallyldimethylammonium halides and also basic (meth)acrylates. Useful examples are copolymers of 1-99 mol %, preferably 30-70 mol %, of acrylamide and/or methacrylamide and 99-1 mol %, preferably 70-30 mol %, of dialkylaminoalkyl acrylates and/or methacrylates such as copolymers of acrylamide and N,N-dimethylethanoyleth acrylate or copolymers of acrylamide and dimethylaminopropyl acrylate. Basic acrylates or methacrylates are preferably present in acid neutralized form or in quaternized form. Quaternization may be effected for example with methyl chloride or with dimethyl sulfate.

[0094] Useful cationic polymers containing amino and/or ammonium groups further include polyallylamines. Polymers of this kind are obtained by homopolymerization of allylamine, preferably in acid neutralized form or in quaternized form, or by copolymerization of allylamine with other monoethenically unsaturated monomers described above as comonomers for N-vinylcarboxamides.

[0095] The cationic polymers have for example K values of from 8 to 300, preferably from 100 to 180 (determined by the method of H. Fikentscher in 5% aqueous sodium chloride solution at 25° C. and a polymer concentration of 0.5% by weight). At pH 4.5, for example, they have a charge density of at least 1, preferably at least 4, meq/g of polyelectrolyte.

[0096] Examples of preferred cationic polymers are polydimethyldiallyl ammonium chloride, polyethyleneimine, polymers containing vinylamine units, copolymers of acrylamide or methacrylamide that contain basic monomers in copolymerized form, polymers containing lysine units or mixtures thereof. Examples of cationic polymers are:

- [0097] copolymers of 50% of vinylpyrrolidone and 50% of trimethylammoniummethyl methacrylate methosulfate, \( M_n = 1000-500000 \);
- [0098] copolymers of 30% of acrylamide and 70% of trimethylammoniummethyl methacrylate methosulfate, \( M_n = 1000-100000 \);
- [0099] copolymers of 70% of acrylamide and 30% of dimethylaminoethylmethacrylamide, \( M_n = 1000-100000 \);
- [0100] copolymers of 50% of hydroxyethyl methacrylate and 50% of 2-dimethylaminoethylmethacrylamide, \( M_n = 1000-500000 \);
- [0101] copolymer of 70% of hydroxyethyl methacrylate and 50% of 2-dimethylaminoethylmethacrylamide; copolymer of 30% of vinylimidazole methylchloride, 50% of dimethylaminoethyl acrylate, 15% of acrylamide, 5% of acrylic acid; \( M_n = 250-250000 \), preferably \( 500-100000 \), and also lysine cocondensates having \( M_n \) molar masses from 250 to 250000, the cocondensable component being selected for example from amines, polyamines, ketone dimers, lactams, alcohols, alkoxyinated amines, alkoxyated alcohols and/or nonproteinogenic amino acids, vinylamine homopolymers, 1-99% hydrolyzed polylvinyformamides, copolymers of vinylformamid and vinyl acetate, vinyl alcohol, vinylpyrrolidone or acrylamide having molar masses of 3000-500000.

- [0102] vinylimidazole homopolymers, vinylimidazole copolymers with vinylpyrrolidone, vinylformamide, acrylamide or vinyl acetate having molar masses of from 5000 to 500000 and also their quaternary derivatives,
- [0103] polyethyleneamines, crosslinked polyethyleneamines or amidated polyethyleneamines having molar masses of from 500 to 3000000,
- [0104] amine-epichlorohydrin polycondensates which contain imidazole, piperazine \( C_2-C_6 \) alkylamines, \( C_1-C_8 \) dialkylamines and/or dimethylaminopropylamine as amine component and have a molar mass of from 500 to 250000, and
- [0105] polymers containing basic (meth)acrylamide or (meth)acrylate ester units, polymers containing basic quaternary (meth)acrylamide or (meth)acrylate ester units having molar masses of from 10000 to 2000000.

[0107] It is also possible to include a minor amount (<10% by weight) of anionic comonomers, for example acrylic acid, methacrylic acid, vinylsulfonic acid or alkali metal salts of the acids mentioned.

[0108] Anionically dispersed particles of reactive modified polymers may be additionally cationically modified, if necessary, by treatment with polyanion metal ions and/or cationic surfactants as well as treatment with cationic polymers. Coating of the particles with polyanion metal ions is obtained when, for example, an aqueous dispersion of an anionically dispersed reactive modified polynomials is admixed with an aqueous solution of at least one water-soluble polyanion metal salt or a water-soluble polyanion metal salt is dissolved therein, the modification of the anionically dispersed reactive modified particles with cationic polymers being effected either before, concurrently with or after this treatment. Useful metal salts include for example the water-soluble salts of Ca, Mg, Ba, Al, Zn, Fe, Cr or mixtures thereof. Other water-soluble metal salts derived for example from Cu, Ni, Co and Mn are useful in principle, but not desired in all applications. Examples of water-soluble metal salts are calcium chloride, calcium acetate, magnesium chloride, aluminum sulfate, aluminum chloride, barium chloride, zinc chloride, zinc sulfate, zinc acetate, iron(II) sulfate, iron(III) chloride, chromium(III) sulfate, copper sulfate, nickel sulfate, cobalt sulfate and manganese sulfate. Cationization is preferably effected using the water-soluble salts of Mg, Ca, Al and Zn.

[0109] There are many industrial uses and uses in the home where the modification of the properties of the textile
and nontextile surfaces with polymer dispersions is important. It is not always possible to effect the modification of the surfaces by impregnating, spraying and brushing processes involving concentrated dispersions. It is frequently desirable to effect the modification by rinsing the surface to be treated with a very dilute liquor that contains an active substance. It is frequently desirable in this context to combine the modifying treatment of the surface with a wash, clean and/or conditioning or impregnation of the surface. Useful surfaces here are in particular surfaces of textile materials such as cotton and cotton blend fabrics. In addition, installed carpeting and furniture covers can be treated according to the invention. The surfaces of textile materials may be modified for example to provide them with water resistance, soil release properties, soil resist properties, improved integrity of the fiber assemblage and protection against chemical or mechanical effects and damage.

[0110] The reactive modified particulate polymers are used for modifying surfaces of the hereinafore exemplified materials as an ingredient in rinsing or care compositions, washing or cleaning compositions, for textile and further, nontextile surfaces. Especially contemplated uses are in washing, cleaning and aftertreating of textiles, leather, wood, floor coverings, glass, ceramics and other surfaces in the home and in the industrial sector.

[0111] The reactive modified particulate polymers are used in the form of a dilute, predominantly aqueous, dispersion. The use takes the form of treatment of the surfaces in washing, cleaning and rinsing liquors to which the polymers are added either directly or by means of a liquid or solid formulation, or in the form of a finely divided application of a liquid formulation, for example by spraying.

[0112] The reactive modified particulate polymers can be used for example as sole active component in aqueous rinsing and care compositions and, depending on the composition of the polymer, provide for example for easier soil release in subsequent wash, reduced soil attachment in the use of the textiles, improved structural integrity of fibers, improved shape retention and structural integrity for fabrics, water repellency on the surface of the washed material and also hand improvement.

[0113] The concentration of the reactive modified particulate polymers when used in a rinsing or care bath, a washing liquor or cleaning bath is for example in the range from 0.0002 to 1% by weight, preferably 0.0005 to 0.25% by weight, particularly preferably from 0.002 to 0.05% by weight.

[0114] The abovementioned applications can in principle be carried out using all reactive modified particulate polymers. Depending on the embodiment, it can be advantageous to select a certain monomer composition to obtain particularly advantageous modifications.

[0115] In a preferred embodiment of the invention, the polymers used contain units derived from cationic monomers and as a result possess enhanced affinity for the surfaces to be treated.

[0116] In a further preferred embodiment, the polymers used contain units derived from anionic monomers and are used together with the cationic polymers, cationic surfactants and/or polyvalent metal cations. The surfaces, for example textile surfaces, are treated with aqueous liquors containing for example from 2.5 to 300 ppm, preferably from 5 to 200 ppm, especially from 10 to 100 ppm, of at least one cationic polymer, up to 5 mmol/l, preferably up to 3.5 mmol/l, of water-soluble salts of polyvalent metals, especially salts of Ca, Mg or Zn, and/or up to 2 mmol/l, preferably up to 0.75 mmol/l, of water-soluble Al salts, and/or up to 600 ppm, preferably up to 300 ppm, of cationic surfactants.

[0117] A further preferred embodiment comprises using alkali-swelling, particularly preferably alkali-soluble, reactive modified polymers. Such polymers are particularly useful for example for improving the soil release of textile and nontextile surfaces. Suitable reactive modified alkali-soluble polymers contain for example

[0118] (a) from 30 to 80% by weight, preferably from 40 to 75% by weight, particularly preferably from 50 to 70% by weight, of at least one sparingly water-soluble or water-insoluble nonionic monomer,

[0119] (b) from 20 to 70% by weight, preferably from 25 to 60% by weight, particularly preferably from 30 to 50% by weight, of at least one carboxyl-containing monomer or salts thereof,

[0120] (c) from 0 to 25% by weight, preferably from 0 to 15% by weight, of one or more sulfon- and/or phosphono-containing monomers or salts thereof,

[0121] (d) from 0 to 30% by weight, preferably from 0 to 15% by weight, of one or more cationic monomers,

[0122] (e) from 0 to 55% by weight, preferably from 0 to 40% by weight, of one or more water-soluble nonionic monomers,

[0123] (f) from 0 to 30% by weight, preferably from 0 to 10% by weight, of one or more multiply ethylenically unsaturated monomers, and

[0124] (g) from 0.1 to 30% by weight, preferably from 0.1 to 10% by weight, of at least one ethylenically unsaturated monomer containing reactive groups.

[0125] Compositions for treating surfaces may have the following composition for example:

[0126] (a) from 0.05 to 40% by weight of a reactive modified particulate polymer whose particle size is from 10 nm to 100 μm,

[0127] (b) from 0 to 10% by weight of one or more cationic polymers,

[0128] (c) from 0 to 30% by weight of one or more water-soluble salts of Mg, Ca, Zn or Al and/or of one or more cationic surfactants,

[0129] (d) from 0 to 80% by weight of one or more customary ingredients such as acids or bases, inorganic builders, organic cobuilders, further surfactants, polymeric dye transfer inhibitors, polymeric soil antideposition agents, soil release polymers, enzymes, complexing agents, corrosion inhibitors, waxes, silicone oils, light stabilizers, dyes, solvents, hydrotropes, thickeners and/or alkanolamines.

[0130] The invention also provides laundry aftertreatment and laundry refreshing compositions and also solid and
liquid laundry detergent formulations that contain the reactive modified particulate polymers.

[0131] Laundry aftertreatment and laundry refreshing compositions contain for example

[0132] (a) from 0.1 to 40% by weight of a reactive modified particulate polymer having a particle size from 10 nm to 100 μm and present as a dispersion in water,

[0133] (b) from 0 to 20% by weight of one or more organic acids such as formic acid, citric acid, adipic acid, succinic acid, oxalic acid or a mixture thereof,

[0134] (c) from 0 to 10% by weight of a cationic polymer,

[0135] (d) from 0 to 30% by weight of one or more water-soluble salts of Mg, Ca, Zn or Al and/or of one or more cationic surfactants,

[0136] (e) from 0 to 30% by weight of one or more nonionic surfactants,

[0137] (f) from 0 to 30% by weight of further customary ingredients such as perfume, silicone oils, other lubricants, film-forming polymers, stabilizers, corrosion control additives, preservatives, bactericides, light stabilizers, dyes, complexing agents, soil antiredeposition agents, soil release polymers, color transfer inhibitors, nonaqueous solvent, hydroptropes, thickeners and/or alkanoamines, and

[0138] (g) water ad 100% by weight.

[0139] Preferred cationic surfactants are selected from the group of the quarternary diesterammonium salts, the quarternary tetraalkylammonium salts, the quarternary diamidoamionium salts, the amidoamine esters and imidazolium salts. These are preferably present in an amount of from 3 to 30% by weight in the laundry refreshers. Examples are quarternary diesterammonium salts which have two C₁₋₄ to C₁₂₋₁₄ alk(en)-ylcarboxyl(mono- to trimethylene) radicals and two C₁₋₄ to C₂₋₅ alkyl or 5 hydroxyalkyl radicals on the quarternary nitrogen atom and, for example, chloride, bromide, methosulfate or sulfate as counterion.

[0140] Quarternary diesterammonium salts further include in particular those which have a C₁₋₄ to C₁₂₋₁₄ alk(en)-ylcarboxyloxytrimethylene radical bearing a C₁₋₄ to C₁₂₋₁₄ alk(en)-ylcarboxy radical on the central carbon atom of the trimethylene group and three C₁₋₄ to C₂₋₅ alkyl or hydroxyalkyl radicals on the quarternary nitrogen atom and, for example, chloride, bromide, methosulfate or sulfate as counterion.

[0141] Quarternary tetraalkylammonium salts are in particular those which have two C₂₋₅ to C₂₋₅ alkyl radicals and two C₂₋₅ to C₂₋₅ alk(en)-yl radicals on the quarternary nitrogen atom and, for example, chloride, bromide, methosulfate or sulfate as counterion.

[0142] Quarternary diamidoammonium salts are in particular those which bear two C₂₋₅ to C₂₋₅ alk(en)-ylcarboxyaminoalkene radicals, a substituent selected from hydrogen, methyl, ethyl and polyoxyethylene having up to 5 oxyethylene units and as fourth radical a methyl group on the quarternary nitrogen atom and, for example, chloride, bromide, methosulfate or sulfate as counterion.

[0143] Amidoamino esters are in particular tertiary amines bearing a C₁₋₄ to C₁₂₋₁₄ alk(en)-ylcarboxylamino(mono- to trimethylene) radical, a C₁₋₄ to C₁₂₋₁₄ alk(en)-ylcarboxyloxy(mono- to trimethylene) radical and a methyl group as substituents on the nitrogen atom.

[0144] Imidazolinium salts are in particular those which bear a C₁₋₄ to C₁₈₋₃₀ alk(en)yl radical in position 2 of the heterocycle, a C₁₋₄ to C₁₂₋₁₄ alk(en)ylcarboxyloxy or aminoalkene radical on the neutral nitrogen atom and hydrogen, methyl or ethyl on the nitrogen atom carrying the positive charge, while counterions here are for example chloride, bromide, methosulfate or sulfate.

[0145] Solid laundry detergent formulations according to the invention contain

[0146] (a) from 0.05 to 20% by weight of a reactive modified particulate polymer having a particle size from 10 nm to 100 μm,

[0147] (b) from 0.1 to 40% by weight of at least one nonionic and/or anionic surfactant,

[0148] (c) from 0 to 50% by weight of one or more inorganic builders,

[0149] (d) from 0 to 20% by weight of one or more organic builders,

[0150] (e) from 0 to 60% by weight of other customary ingredients such as cationic surfactants, standardizers, enzymes, perfume, complexing agents, corrosion inhibitors, bleaches, bleach activators, bleach catalysts, dye transfer inhibitors, soil antiredeposition agents, soil release polymers, dyes, dissolution improvers and/or disintegrants,

[0151] said components (a) to (e) adding up to 100% by weight.

[0152] The solid laundry detergent formulations of the invention are customarily present as a powder, granules, an extrudate or in tablet form.

[0153] Liquid laundry detergent formulations of the invention contain

[0154] (a) from 0.05 to 20% by weight of a reactive modified particulate polymer having a particle size from 10 nm to 100 μm,

[0155] (b) from 0.1 to 40% by weight of at least one nonionic and/or anionic surfactant,

[0156] (c) from 0 to 20% by weight of one or more inorganic builders,

[0157] (d) from 0 to 10% by weight of one or more organic builders,

[0158] (e) from 0 to 40% by weight of other customary ingredients such as cationic surfactants, sodium carbonate, enzymes, perfume, complexing agents, corrosion inhibitors, bleaches, bleach activators, bleach catalysts, dye transfer inhibitors, soil antiredeposition agents, soil release polymers, dyes, nonaqueous solvents, hydroptropes, thickeners and/or alkanoamines, and

[0159] (f) from 0 to 99.85% by weight of water,

[0160] components (a) to (f) adding up to 100% by weight.
Useful anionic surfactants are in particular:

- fatty alcohol sulfates of fatty alcohols having from 8 to 22, preferably from 10 to 18, carbon atoms, for example C_{12} to C_{14}-alcohol sulfates, C_{15} to C_{17} to C_{14} alcohol sulfates, C_{15} to C_{18} alcohol sulfates, laurel sulfate, cetyl sulfate, myristyl sulfate, palmitoyl sulfate, stearyl sulfate and talll alcohol sulfate;
- sulfated alkoxylated C_{6} to C_{22} alcohols (alkyl ether sulfates). Compounds of this kind are prepared for example by first alkoxylating a C_{6} to C_{22} alcohol, preferably a C_{10} to C_{18} alcohol, for example a fatty alcohol, and then sulfating the alkoxylated product. The alkoxylate is preferably carried out using ethylene oxide;
- linear C_{6} to C_{20} alkylbenzenesulfonates (LAS), preferably linear C_{6} to C_{15} alkylbenzenesulfonates and alkyltoluenesulfonates;
- alkanesulfonates such as C_{6} to C_{24} alkanesulfonates, preferably C_{10} to C_{18} alkanesulfonates;
- soaps such as, for example, the sodium and potassium salts of C_{6} to C_{2} carboxylic acids.

Useful inorganic builders are in particular:

- crystalline or amorphous aluminosilicates having ion-exchanging properties such as zeolites in particular. Useful zeolites include in particular zeolites A, X, B, P, MAP and HS in their sodium form or in forms in which sodium has been partly replaced by other cations such as lithium, potassium, calcium, magnesium or ammonium;
- crystalline silicates such as in particular disilicates or sheet silicates, for example β-Na₂Si₂O₅ or β-Na₂Si₂O₇. Silicates can be used in the form of their alkali metal, alkaline earth metal or ammonium salts, preferably as sodium, lithium and magnesium silicates;
- amorphous silicates such as for example sodium metasilicate or amorphous disilicate;
- carbonates and bicarbonates. These can be used in the form of their alkali metal, alkaline earth metal or ammonium salts. Preference is given to sodium, lithium and magnesium carbonates or bicarbonates, especially sodium carbonate and/or sodium bicarbonate;
- polyphosphates such as for example pentasodium triphosphate.

Useful organic cobuilders include in particular low molecular weight, oligomeric or polymeric carboxylic acids.

Useful low molecular weight carboxylic acids include for example citric acid, hydrophobic modified citric acid such as for example agamic acid, malic acid, tartaric acid, glucogenic acid, glutaric acid, succinic acid, imidiodisuccinic acid, oxisuccinic acid, propanetricarboxylic acid, butanetetracarboxylic acid, cyclopentanetetracarboxylic acid, alkyl- and alkylsulfonic acids and aminopolybasic carboxylic acids such as for example nitrotriacetic acid, β-aminoacetic acid, ethylenediaminetetraacetic acid, serinodiacetic acid, isoserinodiacetic acid, N-(2-hydroxyethyl)iminodiacetic acid, ethylenediaminedisuccinic acid and methyl- and ethylygycine diacetic acid;

Useful oligomeric or polymeric carboxylic acids include for example homopolymers of acrylic acid, oligomeric acids, copolymers of maleic acid with acrylic acid, methacrylic acid, C_{2}-C_{6}-olefins such as for example isobutene or longchain α-olefins, vinyl alkyl ethers having C_{1} to C_{6}-alkyl groups, vinyl acetate, vinyl propionate, (meth)acrylic esters of C_{1} to C_{6}-alcohols and styrene. Preference is given to using the homopolymers of acrylic acid and copolymers of acrylic acid with maleic acid. Polyaspartic acids are also useful as organic cobuilders. Oligomeric and polymeric carboxylic acids are used in acid form or as sodium salt.

When the reactive modified particulate polymers are to be cationically modified, this is preferably effected before use in the aqueous treatments, but can also be effected in the course of the manufacture of the aqueous treatments or the use of anionically dispersed particulate polymers having a particle size from 10 nm to 100 μm by for example mixing aqueous dispersions of the contemplated particulate
polymers with the other ingredients of the particular treatment in the presence of cationic polymers and optionally of water-soluble salts of polyvalent metals and/or cationic surfactants.

[0183] In a particular embodiment, reactive modified polymers of anionic character, or formulations containing same, can be added directly to the rinsing, washing or cleaning liquor, provided it is ensured that the liquor contains sufficient amounts of cationic polymers and optionally polyvalent metal ions and/or cationic surfactants in dissolved form. It is possible, for example, to use polymers of anionic character, or formulations containing same, in liquors containing from 2.5 to 300 ppm of cationic polymers and optionally above 0.5 mmol/l, preferably above 1 mmol/l, particularly preferably above 2 mmol/l, of water-soluble salts of Ca, Mg or Zn. When the cationic surfactants are used, they are used for example in concentrations from 50 to 100 ppm, preferably from 75 to 500 ppm, especially from 100 to 300 ppm, in the aqueous liquor.

[0184] The reactive modified polymers of anionic character, or the formulations containing same, may also be added before, after or concurrently with a formulation containing cationic polymers and optionally cationic surfactants.

[0185] Alkali-soluble or alkali-swellable reactive modified particulate polymers provide in particular on cotton and cellulose fibers a substantially higher soil release performance than known water-soluble soil release polymers.

[0186] The invention also provides for the use of reactive modified polymers in finishes for wrinkleproofing cellulosic textiles. Finishes are any liquid formulations which contain the reactive modified polymer, especially in the form of an aqueous polymer dispersion, in dissolved or dispersed form for application to the textile material. The finishes of the invention can be present for example as finishes in the narrower sense in the manufacture of textiles or in the form of an aqueous washing liquor or as a liquid textile treatment. It is thus possible for example to treat textiles with the finish in the course of their manufacture. Textiles which have not been adequately finished, if at all, may be treated with a textile treatment that contains the polymer dispersion for example before or after home laundering, for example during ironing. But it is also possible to treat the textiles with reactive modified polymers in the main wash cycle or after the main wash cycle in the refresher or rinse cycle of the washing machine, for example using the above-described formulations.

[0187] The present invention also provides for the use of the reactive modified polymers, in the manufacture of textiles, textile treatment before and after laundering, main laundry cycle, laundry conditioning rinse cycle and ironing. Different formulations are needed in each case. Examples are the hereinabove described liquid and solid laundry detergents, laundry aftertreatments and laundry refreshers.

[0188] The textiles treated with the reactive modified polymers in the main wash cycle of a washing machine not only wrinkle substantially less than untreated textiles, they are also easier to iron, softer and smoother, more dimensionally and shape stable and, because of the fiber and color protection, look less used, i.e., exhibit less fluff and fewer knots and less color damage or fading, after repeated washing.

[0189] Textiles treated with reactive modified polymers in the rinse or refresher cycle following the main wash cycle and then dried on the line or preferably in a tumble dryer likewise exhibit a very high level of crease resistance and are easier to iron. Crease resistance can be substantially enhanced by briefly ironing the textiles once after drying. The treatment in the conditioning or refresher rinse cycle also has a favorable effect on the shape retention of the textiles. It further inhibits the formation of knots and fluff and suppresses color damage.

[0190] The present invention also provides for the use of the highly branched polymers, especially the highly branched polyurethanes, in the manufacture of textiles, textile treatment before and after laundering, main laundry cycle, laundry conditioning rinse cycle and ironing. Different formulations are needed in each case.

[0191] The treatment before or after laundering may utilize a textile treatment which, as well as the reactive modified polymer dispersed form, contains a surfactant. In this treatment, the cellulosic textiles are for example sprayed with the reactive modified polymers with an add-on which is generally in the range from 0.01 to 10% by weight, preferably in the range from 0.1 to 7% by weight, particularly preferably in the range from 0.3 to 4% by weight, based on the weight of the dry textile material. But the finish may also be applied to the textile material by dipping the textiles into a bath which contains generally from 0.1 to 10% by weight, preferably from 0.3 to 5% by weight, based on the weight of the dry textile material, of the reactive modified particulate polymer in dissolved or dispersed form. The textile material is either dipped only briefly into the bath or else allowed to dwell therein for a period of from 1 to 30 min for example.

[0192] Cellulosic textiles which have been treated with the finish either by spraying or by dipping are if necessary squeezed off and dried. Drying may take place in air or else in a dryer or else by subjecting the treated textile material to hot ironing. The finish becomes fixed on the textile material in the course of drying. The best conditions in each case are readily ascertainable by experimentation. The temperatures for drying, including ironing, are for example in the range from 40 to 150° C. preferably from 60 to 110° C. For ironing, the cotton program of the iron is suitable in particular. Textiles treated with the reactive modified polymers in dispersed form according to the above-described process exhibit an excellent level of wrinkle and crease resistance that is durable to multiple laundering. There is frequently no longer any need to iron the textiles.

[0193] The invention also provides a textile treatment comprising

- [0194] a) from 0.1 to 40% by weight, preferably from 0.5 to 25% by weight, of at least one reactive modified particulate polymer,
- [0195] b) from 0 to 30% by weight of silicones,
- [0196] c) from 0 to 30% by weight of one or more cationic and/or nonionic surfactants,
- [0197] d) from 0 to 60% by weight of further ingredients such as further wetting agents, softeners, lubricants, water-soluble, film-forming and adhesive polymers, scents, dyes, stabilizers, fiber and color
protection additives, viscosity modifiers, soil release additives, corrosion control additives, bactericides, preservatives and spraying assistants, and

[0198] e) from 0 to 99.9% by weight of water,

[0199] components a) to e) adding up to 100% by weight.

[0200] Preferred silicones are amino-containing silicones, which are preferably present in micromulsified form, alkoxylated, especially ethoxylated, silicones, polyalkylene oxidedipolysiloxanes, polyalkylene oxide-aminopolymethylphenylsiloxanes, silicones having quaternary ammonium groups (silicone quats) and silicone surfactants. Useful softeners or lubricants include for example oxidized polyethylene or paraffinic waxes and oils. Useful water-soluble, film-forming and adhesive polymers include for example (co)polymers based on acrylamide, N-vinylpyrrolidone, vinylformamide, N-vinylimidazole, vinylamine, N,N'-dialkylaminooalkyl (meth)acrylates, N,N'-dialkylaminooalkyl(meth)acrylamides, (meth)acrylic acid, alkyl (meth)acrylates and/or vinylsulfonate. The aforementioned basic monomers may also be used in quaternized form.

[0201] A pretreatment formulation to be applied to the textile material by spraying may additionally include a spraying assistant. In some cases, it can also be of advantage to include in the formulation alcohols such as ethanol, isopropanol, ethylene glycol or propylene glycol. Further customary additives are scents, dyes, stabilizers, fiber and color protection additives, viscosity modifiers, soil release additives, corrosion control additives, bactericides and preservatives in customary amounts.

[0202] The textile treatment may generally also be applied by spraying in the course of ironing after laundering. This not only substantially facilitates the ironing, but also imparts sustained wrinkle and crease resistance to the textiles.

[0203] The examples hereinbelow illustrate the invention.

EXAMPLES

[0204] The emulsifiers used in the examples have the following composition:

[0205] Emulsifier 1: 15% by weight solution of sodium lauryl sulfate;

[0206] Emulsifier 2: 40% by weight solution of an ethoxylated and quaternized oleylamine (Lipamine® OK from BASF)

[0207] The particle size distribution was determined using an Autosizer® 2C from Malvern, England. The measurements were carried out at 23° C. Solutions are aqueous solutions, unless otherwise stated. The pH reported in the examples denotes parts by weight based on 100 parts by weight of total monomer.

[0208] Preparation of Polymers

Inventive Example 1

[0209] A glass reactor equipped with anchor stirrer, thermometer, gas inlet tube, dropping funnel and reflux condenser is charged with 12 g of 0.1% by weight solution of sodium persulfate solution initiator, 6 g of a 15% by weight solution of emulsifier 1 and 402 g of water. The contents are heated in a heating bath with stirring while at the same time the air is displaced by the introduction of nitrogen. As soon as the heating bath has reached 75° C, the introduction of nitrogen is discontinued and 4 g of 0.1% by weight sodium persulfate solution and an emulsion of 177 g of ethyl acrylate, 69 g of methacrylic acid, 39 g of acrylic acid, 15 g of glycidyl methacrylate and 22 g of a 15% by weight solution of emulsifier 1 in 400 ml of water are added dropwise over 2 hours. This is followed by 1 hour of supplementary polymerization at 75° C. The batch cooling down to room temperature is admixed with 0.75 g of 30% by weight hydrogen peroxide solution, added all at once, and with a solution containing 0.3 g of ascorbic acid and 0.3 g of iron(II) sulfate in 29.7 g of water, added over 15 minutes.

[0210] The polymer dispersion obtained has the following properties:

<table>
<thead>
<tr>
<th>solvents:</th>
<th>25.8% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>average particle size:</td>
<td>70 nm</td>
</tr>
<tr>
<td>coagulum content:</td>
<td>&lt;1 g</td>
</tr>
<tr>
<td>pH:</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Inventive Example 2

[0211] A glass reactor equipped with anchor stirrer, thermometer, gas inlet tube, dropping funnel and reflux condenser is charged with 12 g of 0.1% by weight solution of sodium persulfate solution initiator, 2.3 g of a 40% by weight solution of emulsifier 2 and 402 g of water. The contents are heated in a heating bath with stirring while at the same time the air is displaced by the introduction of nitrogen. As soon as the heating bath has reached 85° C, the introduction of nitrogen is discontinued and 4 g of 0.1% by weight sodium persulfate solution and an emulsion of 178 g of butyl acrylate, 114 g of methacrylic acid, 15 g of glycidyl methacrylate and 22 g of a 15% by weight solution of emulsifier 1 in 400 ml of water are added dropwise over 2 hours. This is followed by 1 hour of supplementary polymerization at 75° C. The batch cooling down to room temperature is admixed with 0.75 g of 30% by weight hydrogen peroxide solution, added all at once, and with a solution containing 0.3 g of ascorbic acid and 0.3 g of iron(II) sulfate in 29.7 g of water, added over 15 minutes.

[0212] The polymer dispersion obtained has the following properties:

<table>
<thead>
<tr>
<th>solvents:</th>
<th>25.9% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>average particle size:</td>
<td>100 nm</td>
</tr>
<tr>
<td>coagulum content:</td>
<td>&lt;1 g</td>
</tr>
<tr>
<td>pH:</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Inventive Example 3

[0213] A glass reactor equipped with anchor stirrer, thermometer, gas inlet tube, dropping funnel and reflux condenser is charged with 12 g of a 0.1% by weight solution of 2,2'-azobis(2-amidinopropane) dihydrochloride (Wako V 50 from Wako Chemie) as initiator, 2.3 g of a 40% by weight solution of emulsifier 2 and 402 g of water. The contents are heated in a heating bath with stirring while at the same time...
the air is displaced by the introduction of nitrogen. As soon as the heating bath has reached 85°C, the introduction of nitrogen is discontinued and 4 g of the initiator solution and an emulsion of 178 g of butyl acrylate, 114 g of methacrylic acid, 15 g of glycicyl methacrylate and 8.3 g of a 40% by weight solution of emulsifier 1 in 400 ml of water are added dropwise over 2 hours. This is followed by 1 hour of supplementary polymerization at 85°C. The batch cooling down to room temperature is admixed with 0.75 g of 30% by weight hydrogen peroxide solution, added all at once, and with a solution containing 0.3 g of ascorbic acid and 0.3 g of iron(II) sulfate in 29.7 g of water, added over 15 minutes.

[0214] The polymer dispersion obtained has the following properties:

<table>
<thead>
<tr>
<th>Solids content:</th>
<th>25.5% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average particle size:</td>
<td>120 nm</td>
</tr>
<tr>
<td>Coagulum content:</td>
<td>&lt;1 g</td>
</tr>
<tr>
<td>pH:</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Inventive Example 4

[0215] A glass reactor equipped with anchor stirrer, thermometer, gas inlet tube, dropping funnel and reflux condenser is charged with 5.2 g of a 3.8% by weight solution of 2,2'-azobis(2-aminopropane) dihydrochloride (Wako V:50 from Wako Chemie) as initiator, 37.5 g of a 40% by weight solution of emulsifier 2 and 370 g of water. The contents are heated in a heating bath with stirring while at the same time the air is displaced by the introduction of nitrogen. As soon as the heating bath has reached 90°C, the introduction of nitrogen is discontinued and 46.8 g of the initiator feed and an emulsion of 265 g of n-butyl acrylate, 14.5 g of acrylic acid, 135 g of glycicyl methacrylate 85.5 g of dimethylaminopropyl acrylamide, 52 g of 50% by weight sulfuric acid and 37.5 g of 40% by weight solution of emulsifier 2 in 280 ml of water are added dropwise over 2 hours. This is followed by 1 hour of supplementary polymerization at 85°C. The batch cooling down to room temperature is admixed with 25 g of 4% by weight aqueous solution of sodium formaldehyde sulfonic acid (Rongalit® C) and 25 g of a 10% by weight aqueous solution of tert-butyl hydroperoxide over 90 min.

[0216] The polymer dispersion obtained has the following properties:

<table>
<thead>
<tr>
<th>Solids content:</th>
<th>40.6% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average particle size:</td>
<td>120 nm</td>
</tr>
<tr>
<td>Coagulum content:</td>
<td>&lt;1 g</td>
</tr>
<tr>
<td>pH:</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Testing of Soil Release Properties of Polymers Inventive Examples 5-7 and Comparative Example C1

[0217] The soil release properties of the polymer dispersions were tested by conducting washing trials:

[0218] The soil release properties of the polymer dispersions were tested by conducting washing trials:

[0219] Cotton fabrics were prewashed with the anionic polymer dispersions of inventive examples 1 to 3, which contained the polymer in a concentration of 400 ppm, at a pH of 4 in water of 3.0 mmol water hardness and subsequently dried.

[0220] In comparative example C1, the fabric was prewashed at pH 4 in the absence of reactive modified particles.

[0221] In inventive example 7, the fabric was washed with a liquor which contained the reactive modified polymers of inventive example 1 with a coating of polyethyleneimine having a molar mass of 25000. For this, the polyethyleneimine was dissolved in water of 3.0 mmol hardness and the solution adjusted to pH 4.0. This solution was admixed with a 20% by weight polymer dispersion of inventive example 1 having a pH of 4.0. The concentration of the polymer particles in the liquor was 400 ppm and the concentration of the polyethyleneimine was 40 ppm.

[0222] The prewashed fabrics, after drying, were stained with lipstick material and subsequently washed with a commercially available heavy-duty detergent.

Washing Conditions:

[0223] Washing Conditions:

- [0224] washer: Laundor-Meter
- [0225] water hardness: 3.0 mmol/l
- [0226] Ca²⁺/Mg²⁺ ratio: 3:1
- [0227] Prewash:
  - [0228] liquor pH: 4.0
  - [0229] prewash temperature: 20°C
  - [0230] prewash time: 15 min
- [0231] liquor ratio 12.5:1
- [0232] Main Wash:
  - [0233] washing temperature: 40°C
  - [0234] washing time: 30 min
- [0235] liquor ratio 12.5:1
- [0236] After drying, the cotton fabrics were visually rated on a scale from 1 to 5, a rating of 1 denoting an unchanged stain and a rating of 5 being awarded for complete detachment of the lipstick stain.

<table>
<thead>
<tr>
<th>Example</th>
<th>Addition to prewash</th>
<th>Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>without addition</td>
<td>1</td>
</tr>
<tr>
<td>Inv. 5</td>
<td>polymer of inventive example 2</td>
<td>3</td>
</tr>
<tr>
<td>Inv. 6</td>
<td>polymer of inventive example 1</td>
<td>3.5</td>
</tr>
<tr>
<td>Inv. 7</td>
<td>polymer of inventive example 1</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>with coating of polyethyleneimine</td>
<td></td>
</tr>
</tbody>
</table>

[0237] The results of the washing trials show that the use of commercially available heavy duty detergent under the conditions chosen provides virtually no improvement in lipstick soil removal from cotton fabric. Use of the reactive modified polymers, in contrast, provides for a substantial improvement in soil release.
Testing of Hydrophobicizing Properties of Polymers

Inventive Examples 8-10 and Comparative Example C2

The hydrophobicizing properties of the reactive modified polymers were tested by conducting rinsing trials on glass.

Glass platelets measuring 2.5x7.5 cm in area were pretreated at room temperature with an aqueous solution of a nonionic surfactant (200 ppm of C_{12}C_{12} o xo alcohol, alkoxylated with 7 mol of ethylene oxide), after-rinsed with pure water of 3 mmol/l hardness and air dried.

A dispersion of reactive modified polymers as per inventive examples 1 and 2 was prepared, the polymer concentration being 200 ppm, the water hardness 3 mmol and the pH 6.0.

In inventive example 10, an additional 20 ppm of polyethyleneimine having a molar mass of 25000 were present.

The glass platelets were dipped into this dispersion for 10 seconds, then withdrawn and dried at 60° C. for 30 minutes.

The glass platelets thus treated each had applied to them a drop of deionized water and the contact angle was measured. Table 2 shows the contact angles measured.

TABLE 2

<table>
<thead>
<tr>
<th>Example</th>
<th>Addition to rinse liquor</th>
<th>Contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2</td>
<td>without addition</td>
<td>23.9</td>
</tr>
<tr>
<td>Inv. 8</td>
<td>polymer of inventive example 4</td>
<td>42.4</td>
</tr>
<tr>
<td>Inv. 9</td>
<td>polymer of inventive example 3</td>
<td>55.3</td>
</tr>
<tr>
<td>Inv. 10</td>
<td>polymer of inventive example 3 coated with polyethyleneimine of molar mass 25,000</td>
<td>61.2</td>
</tr>
</tbody>
</table>

Wrinkleproofing of Fabric Samples

Inventive Examples 11-14 and Comparative Example C3

Cotton fabrics having the size reported in Table 3 and a basis weight of 160 g/m² were sprayed on both sides with the polymers of inventive examples 1 to 3 in such a way that the add-on was 2%, based on the weight of the dry textile material, and then hot pressed while still slightly moist.

The fabric samples thus treated and, for comparison, untreated fabric samples of the same size were washed in the presence of ballast fabric with a liquid laundry detergent at 40° C. in an automatic domestic machine (load in the range from 1.5 to 3.0 kg) and then tumble dried. A standard washing program and a standard drying program (respectively 40° C. colored wash and the cupboard dry program) were used. After drying, the sheetlike fabric samples were visually rated on the lines of AATCC test method 124, where a rating of 1 indicates that the fabric is highly wrinkled and has many creases and a rating of 5 is awarded to wrinkle- and crease-free fabric.

We claim:

1. A method of treating a surface of a textile or nontextile material, which comprises applying a reactive modified particulate polymer having a particle size from 10 nm to 100 μm from an aqueous dispersion to said surface of said material and drying said material, wherein said reactive modified particulate polymer contains units derived from an ethylenically unsaturated monomer having reactive, crosslinking groups, wherein the crosslinking groups are selected from the group consisting of glycidyl ether, halo-hydryl, carboxylic anhydride, carbonyl chloride, carboxylic ester, isocyanate, vinyl sulfone, N-methylol, aldehyde and imine groups.

2. The method of claim 1 wherein said aqueous dispersion has a polymer content of <1% by weight.

3. The method of claim 1 or 2 wherein said monomer having said reactive, crosslinking groups is selected from the group consisting of glycidyl (meth)acrylate, (meth)acrolein, methacrylic anhydride, 2-(4-ethoxyphenyl)-2-oxazolinyl methacrylate, isobutoxymethacrylamide and maleic anhydride.

4. The method of any of claims 1 to 3 wherein said reactive modified particulate polymer also contains units derived from anionic and/or cationic monomers.

5. The method of any of claims 1 to 4 wherein said reactive modified particulate polymer comprises an anionic, cationic or amphoteric protective colloid or emulsifier at its surface.

6. The method of any of claims 1 to 5 wherein said reactive modified particulate polymer comprises at its surface a protective colloid or emulsifier that contains reactive groups.

7. The method of any of claims 1 to 6 wherein said reactive modified particulate polymer contains anionic groups and/or is dispersed using an anionic protective colloid or emulsifier and comprises a coating of cationic polymer at its surface.

8. A finishing composition for wrinkleproofing a cellulosic textile, comprising a reactive modified particulate polymer as defined in any of claims 1 to 7.

9. The use of a finishing composition comprising a reactive modified particulate polymer as defined in any of
claims 1 to 7 in the manufacture of textiles, textile treatment, main laundry cycle, final laundry rinse cycle and ironing.

10. A composition for treating a surface, comprising

(a) from 0.05 to 40% by weight of a reactive modified particulate polymer whose particle size is from 10 nm to 100 μm as defined in any of claims 1 to 7,

(b) from 0 to 10% by weight of one or more cationic polymers,

(c) from 0 to 30% by weight of one or more water-soluble salts of Mg, Ca, Zn or Al and/or of one or more cationic surfactants,

(d) from 0 to 80% by weight of one or more customary ingredients such as acids or bases, inorganic builders, organic cobuilders, further surfactants, polymeric dye transfer inhibitors, polymeric soil antiredeposition agents, soil release polymers, enzymes, complexing agents, corrosion inhibitors, waxes, silicone oils, light stabilizers, dyes, solvents, hydrotropes, thickeners and/or alkylamines,

said components (a) to (d) adding up to 100% by weight.

11. A laundry aftertreatment or refreshing composition comprising

(a) from 0.1 to 40% by weight of a reactive modified particulate polymer having a particle size from 10 nm to 100 μm as defined in any of claims 1 to 7 and present as a dispersion in water,

(b) from 0 to 20% by weight of one or more organic acids such as formic acid, citric acid, adipic acid, succinic acid, oxalic acid or a mixture thereof,

(c) from 0 to 10% by weight of cationic polymers,

(d) from 0 to 30% by weight of one or more water-soluble salts of Mg, Ca, Zn or Al and/or of one or more cationic surfactants,

(e) from 0 to 30% by weight of one or more nonionic surfactants,

(f) from 0 to 30% by weight of further customary ingredients such as perfume, silicone oil, other lubricants, wetting agents, film-forming polymers, stabilizers, corrosion control additives, preservatives, bactericides, light stabilizers, dye, complexing agents, soil antiredeposition agents, soil release polymers, color transfer inhibitors, nonaqueous solvent, hydrotropes, thickeners and/or alkylamines, and

(g) water ad 100% by weight.

12. A textile treatment composition comprising

a) from 0.1 to 40% by weight of at least one reactive modified particulate polymer, as defined in any of claims 1 to 7,

b) from 0 to 30% by weight of silicones,

c) from 0 to 30% by weight of cationic and/or nonionic surfactants,

d) from 0 to 60% by weight of further ingredients such as further wetting agents, softeners, lubricants, water-soluble, film-forming and adhesive polymers, scents, dyes, stabilizers, fiber and color protection additives, viscosity modifiers, soil release additives, corrosion control additives, bactericides, preservatives and spray assistants, and

c) from 0 to 99.9% by weight of water,
said components a) to e) adding up to 100% by weight.

13. The use of a reactive modified particulate polymer having a particle size from 10 nm to 100 μm as a surface modifying ingredient in a washing, rinsing, refreshing or cleaning composition.

14. The use of claim 14 wherein said reactive modified particulate polymer contains units derived from an ethylenically unsaturated monomer having reactive, crosslinking groups, wherein said reactive, crosslinking groups are selected from the group consisting of glycidyl ether, halohydrin, carboxylic anhydride, carbonyl chloride, carboxylic ester, isocyanate, vinyl sulfate, N-methylol, aldehyde and imine groups.

15. The use of claim 14 wherein said monomer having reactive, crosslinking groups is selected from the group consisting of glycidyl (meth)acrylate, (meth)acrolein, methacrylic anhydride, 2-(4-ethoxyphenyl)-2-oxazolinyl methacrylate, isobutoxymethacrylamide and maleic anhydride.

16. The use of any of claims 13 to 15 wherein said reactive modified particulate polymer also contains units derived from anionic and/or cationic monomers.

17. The use of any of claims 13 to 16 wherein said reactive modified particulate polymer comprises an anionic, cationic or amphoteric protective colloid or emulsifier at its surface.

18. The use of any of claims 13 to 17 wherein said reactive modified particulate polymer comprises at its surface a protective colloid or emulsifier that contains reactive groups.

19. The use of any of claims 13 to 18 wherein said reactive modified particulate polymer contains anionic groups and/or is dispersed using an anionic protective colloid or emulsifier and comprises a coating of cationic polymer at its surface.

20. The use of a reactive modified particulate polymer of any of claims 13 to 19 as a fiber and color protection additive.

21. The use of a reactive modified particulate polymer of any of claims 13 to 19 as a wrinkle control additive for cellulosic textiles.

22. The use of a reactive modified particulate polymer as defined in any of claims 13 to 19 for hydrophobicizing a surface of a textile material.

23. The use of a reactive modified particulate polymer as defined in any of claims 13 to 19 for improving the soil resistance of a surface of a textile material.

24. A solid laundry detergent formulation comprising

(a) from 0.05 to 20% by weight of a reactive modified particulate polymer having a particle size from 10 nm to 100 μm,

(b) from 0.1 to 40% by weight of at least one nonionic and/or anionic surfactant,

(c) from 0 to 50% by weight of one or more inorganic builders,

(d) from 0 to 20% by weight of one or more organic cobuilders,
(e) from 0 to 60% by weight of other customary ingredients such as cationic surfactants, standardizers, enzymes, perfume, complexing agents, corrosion inhibitors, bleaches, bleach activators, bleach catalysts, dye transfer inhibitors, soil antiredeposition agents, soil release polyesters, dyes, dissolution improvers and/or disintegrants,

said components (a) to (e) adding up to 100% by weight.

25. A liquid laundry detergent formulation comprising
(a) from 0.05 to 20% by weight of a reactive modified particulate polymer having a particle size from 10 nm to 100 μm,
(b) from 0.1 to 40% by weight of at least one nonionic and/or anionic surfactant,
(c) from 0 to 20% by weight of one or more inorganic builders,
(d) from 0 to 10% by weight of one or more organic cobuilders,
(e) from 0 to 40% by weight of other customary ingredients such as cationic surfactants, sodium carbonate, enzymes, perfume, complexing agents, corrosion inhibitors, bleaches, bleach activators, bleach catalysts, dye transfer inhibitors, soil antiredeposition agents, soil release polyesters, dyes, nonaqueous solvents, hydrotopes, thickeners and/or alkanolamines, and
(f) from 0 to 99.85% by weight of water,
said components (a) to (f) adding up to 100% by weight.

* * * * *