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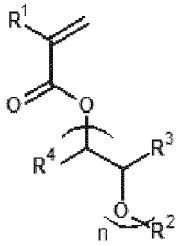
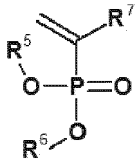
(54) **DETERGENT HAVING IMPROVED PERFORMANCE**

(57) The present invention is related to the use of polymers, obtainable by radical-induced copolymerization of monomers according to formula I,



(I)

in which, independently from each other, R^1 and R^2 is H or an alkyl group with 1 to 4 C-atoms, R^3 and R^4 is H or a methyl group, and n is a number from 1 to 200, with monomers according to formula II,



(II)

in which, independently from each other, R^5, R^6 and R^7 is H or an alkyl group with 1 to 4 C-atoms with the proviso that at least one of R^5 and R^6 is H, and with branching monomers according to formula III,

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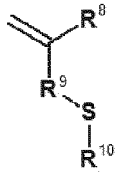


(III)

in which
R^8 is H or or an alkyl group with 1 to 4 C-atoms,
R^9 is -C(O)-O-R^{11}-, -C(O)-N$R^{11}R^{12}$-, -O-R^{11}-, an arylene group, a linear or branched alkylene group with 1 to 20 C-atoms, or -$(CH_2$-CHR^{13}-$O)_m$-,
R^{10} is -C(S)-S-R^{14}, -C(S)-R^{15}, -C(S)-N$R^{16}R^{17}$, or -C(S)-O-R^{18}
R^{11} is a linear or branched alkylene group with 1 to 20 C-atoms, or -$(CH_2$-CHR^{13}-$O)_m$-,
R^{12} is H or a linear or branched alkylene group with 1 to 20 C-atoms, or -$(CH_2$-CHR^{13}-$O)_m$-,
R^{13} is H or a methyl group,
R^{14} is a linear or branched alkylene group with 1 to 20 C-atoms, or a pyrrolidone group,
R^{15} is an aryl group or a linear or branched alkylene group with 1 to 20 C-atoms, or a pyrrolidone group,
R^{16}, R^{17} and R^{18} are, independently from each other, H, an aryl group, a linear or branched alkyl group with 1 to 20 C-atoms, or, -$(CH_2$-CHR^{13}-$O)_m$-H, and
m is a number of from 1 to 20, to improve the cleaning performance of detergents.

Description

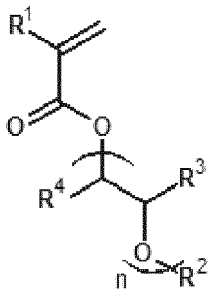
[0001] The present invention is related to the use of polymers comprising phosphono groups and polyoxyalkylene side chains in washing and cleaning agents to improve their cleaning performance, in particular with regard to bleach-sensitive stains.

[0002] While formulating powdered washing and cleaning agents containing bleaching agents no longer presents any problems nowadays, formulating stable, liquid washing and cleaning agents containing bleaching agents is still problematic. Accordingly, the customary absence of bleaching agent in liquid washing and cleaning agents means that stains that would normally be removed, in particular because of the bleach content, are frequently only inadequately removed. A similar problem exists with bleach-free color washing agents from which the bleaching agent is omitted so as to protect the dyes in the textiles and to prevent them from fading. In the absence of a bleaching agent there is the additional difficulty that rather than removing the stains, which would normally be removed by the bleaching agent, the washing process by contrast frequently even intensifies the stain and/or makes it more difficult to remove, a fact that is attributable not least to initiated chemical reactions consisting for example in the polymerization of certain dyes contained in the stains.

[0003] Such problems of difficult removal of bleach-sensitive stains occur in particular with stains containing polymerizable dyes. These are mostly red- to blue-colored stains. The polymerizable substances are above all polyphenolic dyes, preferably flavonoids, in particular from the class of anthocyanidins or anthocyanins. The stains can be caused in particular by food products or drinks containing corresponding dyes. In particular, the stains can be marks from fruit or vegetables or red wine marks containing red and/or blue dyes, in particular polyphenolic dyes, above all those from the class of anthocyanidins or anthocyanins.

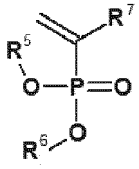
[0004] Surprisingly it has been found that the cleaning performance of the washing or cleaning agent with respect of stains, in particular with regard to bleach-sensitive stains, can be markedly improved through the use of branched copolymers that comprise phosphono groups and polyoxyalkylene side chains.

[0005] Therefore, the present invention firstly provides the use of copolymers, obtainable by radical-induced copolymerization of monomers according to formula I,



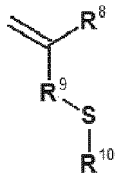
(I)

in which, independently from each other, R^1 and R^2 is H or an alkyl group with 1 to 4 C-atoms, R^3 and R^4 is H or a methyl group, and n is a number from 1 to 200, preferably from 1 to 50,
with monomers according to formula II,



(II)

in which, independently from each other, R^5, R^6 and R^7 is H or an alkyl group with 1 to 4 C-atoms with the proviso that at least one of R^5 and R^6 is H, and
with branching monomers according to formula III,



(III)

in which

R^8 is H or or an alkyl group with 1 to 4 C-atoms,
R^9 is -C(O)-O-R^{11}-, -C(O)-N$R^{11}R^{12}$-, -O-R^{11}-, an arylene group, a linear or branched alkylene group with 1 to 20 C-atoms, or -$(CH_2$-CHR^{13}-$O)_m$-,
R^{10} is -C(S)-S-R^{14}, -C(S)-R^{15}, -C(S)-N$R^{16}R^{17}$, or -C(S)-O-R^{18}
R^{11} is a linear or branched alkylene group with 1 to 20 C-atoms, or -$(CH_2$-CHR^{13}-$O)_m$-,
R^{12} is H or a linear or branched alkylene group with 1 to 20 C-atoms, or -$(CH_2$-CHR^{13}-$O)_m$-,
R^{13} is H or a methyl group,
R^{14} is a linear or branched alkylene group with 1 to 20 C-atoms, or a pyrrolidone group,
R^{15} is an aryl group or a linear or branched alkylene group with 1 to 20 C-atoms, or a pyrrolidone group,
R^{16}, R^{17} and R^{18} are, independently from each other, H, an aryl group, a linear or branched alkyl group with 1 to 20 C-atoms, or, -$(CH_2$-CHR^{13}-$O)_m$-H, and
m is a number of from 1 to 20
in washing and cleaning detergents to improve the cleaning performance, especially with respect to bleach-sensitive stains, in particular for the improved removal of stains containing polymerizable substances, in particular polymerizable dyes, wherein the polymerizable dyes are preferably polyphenolic dyes, in particular flavonoids, above all anthocyanidins or anthocyanins or oligomers of said compounds. These are especially red- to blue-colored stains, in particular marks from fruit or vegetables or red wine marks containing red- to blue-colored dyes, in particular also stains from food products or drinks containing corresponding dyes.

[0006] The present invention secondly provides for washing and cleaning detergents comprising said copolymers.

[0007] "Bleach-sensitive stains" are understood to be stains which normally are removed, at least partially, by the action of conventional bleaching agents or bleaching agent systems, such as sodium perborate or sodium percarbonate, often used as a system in combination with so-called bleach activators such as tetraacetylethylenediamine or sodium nonanoyloxy benzene sulfonate, commonly used in detergents.

[0008] "Red- to blue-colored stains" are understood to be stains which can have a color from the red to blue color spectrum. Thus, in addition to stains in the colors red or blue they include in particular stains in intermediate colors, in particular violet, lilac, purple or pink, in other words stains having a red, violet, lilac, purple, pink or blue tone, without themselves essentially consisting entirely of that color. The specified colors can in particular also be light or dark, i.e. possible colors include in particular light and dark red and light and dark blue. The stains to be preferably removed according to the invention can be caused in particular by cherries, red grapes, pomegranate, chokeberry, plums, sea buckthorn, acai or berries, in particular by redcurrants or blackcurrants, elderberries, blackberries, raspberries, blueberries, lingonberries, cowberries, strawberries or bilberries, red cabbage, blood orange, eggplant, black carrot, red- or blue-fleshed potatoes or red onions.

[0009] Monomers according to formula I may be obtained by reacting unsaturated carboxylic acids $H_2C=C(R^1)COOH$ or their reactive derivatives, such as acid chlorides, with polyalkylene glycols or polyalkylene glycol monoethers HO-$(CHR^3$-CHR^4-$O)_n$-R^2 to form the corresponding esters. The index n in formula I as well as the index m in formula III may be an integer or a fraction. Preferably in the monomers according to formula I R^1, R^2, R^3 and R^4, independently from each other, are H or methyl groups, wherein, more preferred, R^3 and R^4 are not both methyl groups. In the monomers according to formula II, preferably both R^5 and R^6 are H, and/or R^7 is H. If in formula III R^{12} is a linear or branched alkylene group with 1 to 20 C-atoms or -$(CH_2$-CHR^{13}-$O)_m$-, the monomers comprise two chain transfer moieties S-R^{10}. Employing monomers of general formula III results in the formation of hyperbranched copolymers.

[0010] The copolymers used according to the invention are obtainable by free-radical polymerization of the ethylenically unsaturated monomers of the general formulae I, II, and III. They may contain the monomeric units stemming from the monomers of one of said general formulae in random distribution or they may comprise blocks each made up of one of the different monomeric units. Preferably, the copolymers used according to the invention consist only of monomeric units stemming from monomers of the given formulae, apart from portions originating from customary radical chain initiators and terminators.

[0011] The copolymer used according to the invention preferably has an average molar mass in the range from 1000 g/mol to 500,000 g/mol, in particular from 1000 g/mol to 250,000 g/mol. The average molar masses specified here and below, optionally for other polymers, are number-average molar masses M_n, which can be determined in principle by gel permeation chromatography using an RI detector, the measurement conveniently being performed against an external standard. It preferably comprises units stemming from monomers according to formula II and units stemming from monomers according to formula III in molar ratios in the range of from 1:1 to 100:1, preferably from 10:1 to 50:1.

[0012] The copolymers defined above are preferably used in washing or cleaning detergents in an amount in a range of from 0.01 wt.% to 5 wt.%, in particular in a range of from 0.1 wt.% to 2 wt.%, wherein here and below the figures given as "wt.%"refer in each case to the weight of the total washing or cleaning detergent.

[0013] The washing or cleaning detergent can be present in any presentation form that is established according to the prior art and/or any convenient presentation form. These include for example solid, powdered, liquid, gel or paste presentation forms, optionally also consisting of a plurality of phases, compressed or not compressed; they also include, for example: extrudates, granules, tablets or pouches, packed both in bulk containers and in portions.

[0014] In a preferred embodiment, the use according to the invention occurs in a washing or cleaning detergent containing no bleaching agent. This is understood to mean that the detergent according to the invention contains no bleaching agent in the narrower sense, in other words hydrogen peroxide or substances yielding hydrogen peroxide in aqueous systems; it preferably also contains no bleach activators and/or bleach catalysts.

[0015] In a more preferred embodiment the detergent according to the invention is a liquid detergent for washing textiles.

[0016] In a further more preferred embodiment the detergent according to the invention is a powdered color detergent, in other words a powdered detergent for washing colored textiles.

[0017] The washing and cleaning detergents according to the invention can moreover contain other conventional constituents of washing and cleaning agents, in particular textile washing agents, selected in particular from the group of builders, surfactants, polymers, enzymes, disintegrating agents, scents and perfume carriers.

[0018] The builders include in particular zeolites, silicates, carbonates, organic cobuilders and - provided that there are no ecological prejudices against their use - phosphates.

[0019] The finely crystalline, synthetic zeolite containing bound water is preferably zeolite A and/or zeolite P. One example of a suitable zeolite P is zeolite MAP® (a commercial product from Crosfield). Zeolite X and mixtures of zeolite A, X and/or P are also suitable, however. A co-crystallisate of zeolite X and zeolite A (approx. 80 wt.% zeolite X), for example, which can be described by the formula

$$n\ Na_2O \cdot (1\text{-}n)K_2O \cdot Al_2O_3 \cdot (2 - 2.5)\ SiO_2 \cdot (3.5 - 5.5)\ H_2O$$

is commercially available and can be used in the context of the present invention. The zeolite can be used both as a builder in a granular compound and also to achieve a type of "powdering" of a granular mixture, preferably of a compressible mixture, wherein both methods of incorporating the zeolite into the pre-mixture are conventionally used. Zeolites can have an average particle size of less than 10 μm (volume distribution; measurement method: Coulter counter) and preferably contain 18 wt.% to 22 wt.%, in particular 20 wt.% to 22 wt.%, of bound water.

[0020] Crystalline layered silicates of the general formula $NaMSi_xO_{2x+1} \cdot y\ H_2O$ can also be used, in which M denotes sodium or hydrogen, x is a number from 1.9 to 22, preferably from 1.9 to 4, more preferred values for x being 2, 3 or 4, and y denotes a number from 0 to 33, preferably from 0 to 20. The crystalline layered silicates of the formula $NaMSi_xO_{2x+1} \cdot y\ H_2O$ are sold for example by Clariant GmbH (Germany) under the trade name Na-SKS. Examples of these silicates are Na-SKS-1 ($Na_2Si_{22}O_{45} \cdot x\ H_2O$, kenyaite), Na-SKS-2 ($Na_2Si_{14}O_{29} \cdot x\ H_2O$, magadiite), Na-SKS-3 ($Na_2Si_8O_{17} \cdot x\ H_2O$) or Na-SKS-4 ($Na_2Si_4O_9 \cdot x\ H_2O$, makatite).

[0021] Crystalline phyllosilicates of the formula $NaMSi_xO_{2x+1} \cdot y\ H_2O$ in which x denotes 2 are preferred. In particular, both β- and δ-sodium disilicates $Na_2Si_2O_5 \cdot y\ H_2O$ and moreover above all Na-SKS-5 (α-$Na_2Si_2O_5$), Na-SKS-7(β-$Na_2Si_2O_5$, natrosilite), Na-SKS-9($NaHSi_2O_5 \cdot H_2O$), Na-SKS-10 ($NaHSi_2O_5 \cdot 3\ H_2O$, kanemite), Na-SKS-11 (t-$Na_2Si_2O_5$) and Na-SKS-13 ($NaHSi_2O_5$) are suitable, but in particular Na-SKS-6(δ-$Na_2Si_2O_5$). Washing or cleaning agents preferably contain a proportion by weight of the crystalline layered silicate of the formula $NaMSi_xO_{2x+1} \cdot y\ H_2O$ from 0.1 wt.% to 20 wt.%, preferably from 0.2 wt.% to 15 wt.% and in particular from 0.4 wt.% to 10 wt.%.

[0022] Amorphous sodium silicates having an $Na_2O : SiO_2$ modulus from 1:2 to 1:3.3, preferably from 1:2 to 1:2.8 and in particular from 1:2 to 1:2.6, which preferably have a delayed solubility and secondary washing properties, can also be used. The delayed solubility in comparison to conventional amorphous sodium silicates can be brought about in various ways, for example by surface treatment, compounding, compacting/compression or by overdrying. The term "amorphous" is understood to mean that in X-ray diffraction experiments the silicates do not yield sharp X-ray reflexes, as is typical of crystalline substances, but rather at most give rise to one or more maxima of the scattered X-ray radiation having a width of several degree units of the diffraction angle.

[0023] Alternatively, or in combination with the aforementioned amorphous sodium silicates, X-ray-amorphous silicates can be used whose silicate particles yield intergrown or even sharp diffraction maxima in electron diffraction experiments. This should be interpreted to mean that the products have microcrystalline regions of ten to some hundred nm in size, with values of up to max. 50 nm and in particular up to max. 20 nm being preferred. Such X-ray-amorphous silicates likewise have a delayed solubility in comparison to the conventional water glasses. Compressed/compacted amorphous silicates, compounded amorphous silicates and overdried X-ray-amorphous silicates are preferred in particular.

[0024] If present, this (these) silicate(s), preferably alkali silicates, more preferably crystalline or amorphous alkali disilicates, are included in washing or cleaning agents in amounts from 3 wt.% to 60 wt.%, preferably from 8 wt.% to 50 wt.% and in particular from 20 wt.% to 40 wt.%.

[0025] A use of the generally known phosphates as builder substances is also possible, provided that such a use is not to be avoided on ecological grounds. Of the many commercially available phosphates, the alkali metal phosphates,

with particular preference for pentasodium or pentapotassium triphosphate (sodium or potassium tripolyphosphate), have the greatest significance in the washing and cleaning agents industry.

[0026] Alkali metal phosphates is the summary term for the alkali metal (in particular sodium and potassium) salts of the various phosphoric acids, among which it is possible to differentiate between metaphosphoric acids $(HPO_3)_n$ and orthophosphoric acids H_3PO_4 and higher-molecular-weight representatives. The phosphates combine several advantages: they act as alkali carriers, prevent limescale deposits on machine parts or limescale encrustations in fabrics and in addition contribute to the cleaning performance. Particularly important phosphates in industry are pentasodium triphosphate, $Na_5P_3O_{10}$ (sodium tripolyphosphate) and the corresponding potassium salt pentapotassium triphosphate, $K_5P_3O_{10}$ (potassium tripolyphosphate). Sodium potassium tripolyphosphates are also preferably used. If phosphates are used in washing or cleaning agents, preferred agents contain this (these) phosphate(s), preferably alkali metal phosphate(s), more preferably pentasodium or pentapotassium triphosphate (sodium or potassium tripolyphosphate), in amounts from 5 wt.% to 80 wt.%, preferably from 15 wt.% to 75 wt.% and in particular from 20 wt.% to 70 wt.%.

[0027] Alkali carriers can also be used. Alkali carriers include for example alkali metal hydroxides, alkali metal carbonates, alkali metal hydrogen carbonates, alkali metal sesquicarbonates, the cited alkali silicates, alkali metasilicates and mixtures of the aforementioned substances, with alkali carbonates, in particular sodium carbonate, sodium hydrogen carbonate or sodium sesquicarbonate, preferably being used. A builder system containing a mixture of tripolyphosphate and sodium carbonate can be more preferred. Owing to their low chemical compatibility with the other ingredients of washing or cleaning agents in comparison to other builder substances, the alkali metal hydroxides are conventionally used in only small amounts, preferably in amounts below 10 wt.%, preferably below 6 wt.%, more preferably below 4 wt.% and in particular below 2 wt.%. Agents containing relative to their total weight less than 0.5 wt.% and in particular no alkali metal hydroxides are more preferred. The use of carbonate(s) and/or hydrogen carbonate(s), preferably alkali carbonate(s), more preferably sodium carbonate, in amounts from 2 wt.% to 50 wt.%, preferably from 5 wt.% to 40 wt.% and in particular from 7.5 wt.% to 30 wt.%, is preferred.

[0028] Polycarboxylates/polycarboxylic acids, polymeric polycarboxylates, aspartic acid, polyacetals, dextrins and phosphonates can be mentioned in particular as organic cobuilders. The polycarboxylic acids, which can be used in the form of the free acid and/or its sodium salts, polycarboxylic acids being understood to be those carboxylic acids carrying more than one acid function, can be used for example. These are for example citric acid, adipic acid, succinic acid, glutaric acid, malic acid, tartaric acid, maleic acid, fumaric acid, sugar acids, aminocarboxylic acids, nitrilotriacetic acid (NTA), provided that such a use is not to be opposed on ecological grounds, and mixtures thereof. In addition to their builder action, the free acids typically also have the characteristic of an acidifying component and are thus also used to establish a lower and milder pH in washing or cleaning agents. Citric acid, succinic acid, glutaric acid, adipic acid, gluconic acid and any mixtures thereof are to be cited here in particular. Also suitable as builders are polymeric polycarboxylates, such as for example the alkali metal salts of polyacrylic acid or polymethacrylic acid, for example those having a relative molar mass from 500 g/mol to 70,000 g/mol. Polyacrylates, which preferably have a molar mass from 2000 g/mol to 20,000 g/mol, are suitable in particular. Of this group, owing to their superior solubility, preference can in turn be given to the short-chain polyacrylates having molar masses from 2000 g/mol to 10,000 g/mol and more preferably from 3000 g/mol to 5000 g/mol. Also suitable are copolymeric polycarboxylates, in particular those of acrylic acid with methacrylic acid and of acrylic acid or methacrylic acid with maleic acid. Copolymers of acrylic acid with maleic acid containing 50 wt.% to 90 wt.% of acrylic acid and 50 wt.% to 10 wt.% of maleic acid have proved to be particularly suitable. Their relative molar mass, relative to free acids, is generally 2000 g/mol to 70,000 g/mol, preferably 20,000 g/mol to 50,000 g/mol and in particular 30,000 g/mol to 40,000 g/mol. To improve their solubility in water the polymers can also contain allyl sulfonic acids, such as for example allyloxybenzenesulfonic acid and methallyl sulfonic acid, as monomers. The (co)polymeric polycarboxylates can be used as a solid or in aqueous solution. The content of (co)polymeric polycarboxylates in washing or cleaning agents is preferably 0.5 wt.% to 20 wt.% and in particular 3 wt.% to 10 wt.%.

[0029] Biodegradable polymers consisting of more than two different monomer units are also preferred in particular, for example those containing as monomers salts of acrylic acid and maleic acid and vinyl alcohol or vinyl alcohol derivatives or those containing as monomers salts of acrylic acid and 2-alkyl allyl sulfonic acid and sugar derivatives. Further preferred copolymers are those having acrolein and acrylic acid/acrylic acid salts or acrolein and vinyl acetate as monomers. Also to be mentioned as further preferred builder substances are polymeric amino dicarboxylic acids, the salts thereof or the precursor substances thereof. Polyaspartic acids or salts thereof are more preferred.

[0030] Further suitable builder substances are polyacetals, which can be obtained by reacting dialdehydes with polyol carboxylic acids having 5 to 7 C atoms and at least 3 hydroxyl groups. Preferred polyacetals are obtained from dialdehydes such as glyoxal, glutaraldehyde, terephthalaldehyde and mixtures thereof and from polyol carboxylic acids such as gluconic acid and/or glucoheptonic acid.

[0031] Further suitable organic builder substances are dextrins, for example oligomers or polymers of carbohydrates, which can be obtained by partial hydrolysis of starches. The hydrolysis can be performed by conventional methods, for example acid- or enzyme-catalyzed methods. The hydrolysis products preferably have average molar masses in the range from 400 g/mol to 500,000 g/mol. A polysaccharide having a dextrose equivalent (DE) in the range from 0.5 to

40, in particular from 2 to 30, is preferred, wherein DE is a commonly used measure for the reducing action of a polysaccharide in comparison to dextrose, which has a DE of 100. Both maltodextrins having a DE of between 3 and 20 and dry glucose syrups having a DE of between 20 and 37 and also yellow dextrins and white dextrins having elevated molar masses in the range from 2000 g/mol to 30,000 g/mol can be used. The oxidized derivatives of such dextrins are their reaction products with oxidizing agents which are capable of oxidizing at least one alcohol function of the saccharide ring to the carboxylic acid function.

[0032] Oxydisuccinates and other derivatives of disuccinates, preferably ethylenediamine disuccinate, are further additional suitable cobuilders. Ethylenediamine-N,N'-disuccinate (EDDS) is preferably used here in the form of its sodium or magnesium salts. Also preferred in this context are glycerol disuccinates and glycerol trisuccinates. If desired, suitable amounts to be used, in particular in formulations containing zeolites and/or silicates, are 3 wt.% to 15 wt.%.

[0033] Further organic cobuilders which can be used are for example acetylated hydroxycarboxylic acids or salts thereof which can optionally also be present in the lactone form and which contain at least four carbon atoms and at least one hydroxyl group as well as a maximum of two acid groups.

[0034] Furthermore, all compounds which are capable of forming complexes with alkaline-earth ions can be used as builders.

[0035] Washing and cleaning agents can contain non-ionic, anionic, cationic and/or amphoteric surfactants.

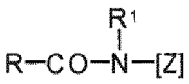
[0036] All non-ionic surfactants known to the person skilled in the art can be used as non-ionic surfactants. Washing or cleaning agents contain to particular advantage non-ionic surfactants from the group of alkoxylated alcohols. Alkoxylated, advantageously ethoxylated, in particular primary alcohols having preferably 8 to 18 C atoms and on average 1 to 12 mol of ethylene oxide (EO) per mol of alcohol are preferably used as non-ionic surfactants, in which the alcohol residue can be linear or preferably methyl-branched in the 2-position or can contain linear and methyl-branched residues in the mixture, such as are conventionally present in oxoalcohol residues. However, alcohol ethoxylates having linear residues obtained from alcohols of native origin having 12 to 18 C atoms, for example from coconut, palm, tallow or oleyl alcohol, and on average 2 to 8 mol of EO per mol of alcohol are preferred in particular. The preferred ethoxylated alcohols include, for example, C_{12-14} alcohols having 3 EO or 4 EO, C_{9-11} alcohol having 7 EO, C_{13-15} alcohols having 3 EO, 5 EO, 7 EO or 8 EO, C_{12-18} alcohols having 3 EO, 5 EO or 7 EO and mixtures thereof, such as mixtures of C_{12-14} alcohol having 3 EO and C_{12-18} alcohol having 5 EO. The specified degrees of ethoxylation are statistical averages which for an individual product can correspond to a whole number or a fraction. Preferred alcohol ethoxylates have a narrow homolog distribution (narrow-range ethoxylates, NRE).

[0037] Alternatively, or in addition to these non-ionic surfactants, fatty alcohols having more than 12 EO can also be used. Examples thereof are tallow fatty alcohol having 14 EO, 25 EO, 30 EO or 40 EO. Alkyl glycosides of the general formula $RO(G)_x$ can moreover be used as further non-ionic surfactants, in which R corresponds to a primary straight-chain or methyl-branched aliphatic residue, in particular one methyl-branched in the 2-position, having 8 to 22, preferably 12 to 18 C atoms, and G is the symbol denoting a glycose unit having 5 or 6 C atoms, preferably glucose. The degree of oligomerization x, which indicates the distribution of monoglycosides and oligoglycosides, is any number between 1 and 10; x is preferably 1.2 to 1.4.

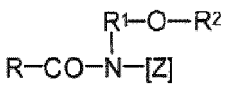
[0038] Another class of preferably used non-ionic surfactants, which are used either as the only non-ionic surfactant or in combination with other non-ionic surfactants, is alkoxylated, preferably ethoxylated or ethoxylated and propoxylated, fatty acid alkyl esters, preferably having 1 to 4 carbon atoms in the alkyl chain.

[0039] Non-ionic surfactants of the amine oxide type, for example N-cocoalkyl-N,N-dimethyl amine oxide and N-tallow alkyl-N,N-dihydroxyethyl amine oxide, and of the fatty acid alkanol amide type can also be used. The amount of these non-ionic surfactants is preferably no more than that of the ethoxylated fatty alcohols, in particular no more than half that.

[0040] Further suitable surfactants are polyhydroxy fatty acid amides of the formula



in which R denotes an aliphatic acyl residue having 6 to 22 carbon atoms, R^1 denotes hydrogen, an alkyl or hydroxyalkyl residue having 1 to 4 carbon atoms and [Z] denotes a linear or branched polyhydroxyalkyl residue having 3 to 10 carbon atoms and 3 to 10 hydroxyl groups. The polyhydroxy fatty acid amides are known substances which can conventionally be obtained by reductive amination of a reducing sugar with ammonia, an alkyl amine or an alkanol amine and subsequent acylation with a fatty acid, a fatty acid alkyl ester or a fatty acid chloride. The group of polyhydroxy fatty acid amides also includes compounds of the formula



in which R denotes a linear or branched alkyl or alkenyl residue having 7 to 12 carbon atoms, R^1 denotes a linear, branched or cyclic alkyl residue or an aryl residue having 2 to 8 carbon atoms and R^2 denotes a linear, branched or cyclic alkyl residue or an aryl residue or an oxyalkyl residue having 1 to 8 carbon atoms, C_{1-4} alkyl or phenyl residues being preferred, and [Z] denotes a linear polyhydroxyalkyl residue, whose alkyl chain is substituted with at least two hydroxyl groups, or alkoxylated, preferably ethoxylated or propoxylated derivatives of this residue. [Z] is preferably obtained by reductive amination of a reduced sugar, for example glucose, fructose, maltose, lactose, galactose, mannose or xylose. The N-alkoxy- or N-aryloxy-substituted compounds can be converted into the desired polyhydroxy fatty acid amides by reaction with fatty acid methyl esters in the presence of an alkoxide as catalyst.

[0041] Non-ionic surfactants from the group of alkoxylated alcohols, more preferably from the group of mixed alkoxylated alcohols and in particular from the group of EO/AO/EO non-ionic surfactants, or PO/AO/PO non-ionic surfactants, especially PO/EO/PO non-ionic surfactants, are more preferred in cleaning agents. Such PO/EO/PO non-ionic surfactants are characterized by good foam control.

[0042] Surfactants of the sulfonate and sulfate type for example are used as anionic surfactants. Suitable surfactants of the sulfonate type are preferably C_{9-13} alkylbenzene sulfonates, olefin sulfonates, i.e. mixtures of alkene and hydroxyalkane sulfonates, and disulfonates, such as are obtained for example from C_{12-18} monoolefins having a terminal or internal double bond by sulfonation with gaseous sulfur trioxide and subsequent alkaline or acid hydrolysis of the sulfonation products. Also suitable are alkane sulfonates obtained from C_{12-18} alkanes, for example by sulfochlorination or sulfoxidation with subsequent hydrolysis or neutralization. Likewise suitable are the esters of α-sulfo fatty acids (ester sulfonates), for example the α-sulfonated methyl esters of hydrogenated coconut, palm kernel or tallow fatty acids.

[0043] Further suitable anionic surfactants are sulfonated fatty acid glycerol esters. Fatty acid glycerol esters are understood to be the mono-, di- and triesters and mixtures thereof, such as are obtained in the production by esterification of a monoglycerol with 1 to 3 mol of fatty acid or in the interesterification of triglycerides with 0.3 to 2 mol of glycerol. Preferred sulfonated fatty acid glycerol esters are the sulfonation products of saturated fatty acids having 6 to 22 carbon atoms, for example of hexanoic acid, octanoic acid, decanoic acid, myristic acid, lauric acid, palmitic acid, stearic acid or docosanoic acid.

[0044] The alkali and in particular the sodium salts of the sulfuric acid semi-esters of C_{12}-C_{18} fatty alcohols, for example of coconut fatty alcohol, tallow fatty alcohol, lauryl, myristyl, cetyl or stearyl alcohol, or of C_{10}-C_{20} oxoalcohols and the semi-esters of secondary alcohols of those chain lengths are preferred as alk(en)yl sulfates. Also preferred are alk(en)yl sulfates of the specified chain length containing a synthetic, straight-chain alkyl residue produced on a petrochemical basis, which have an analogous degradation behavior to the appropriate compounds based on fat chemistry raw materials. From a detergent perspective the C_{12}-C_{16} alkyl sulfates and C_{12}-C_{15} alkyl sulfates and C_{14}-C_{15} alkyl sulfates are preferred.

[0045] The sulfuric acid monoesters of the straight-chain or branched C_{7-21} alcohols ethoxylated with 1 to 6 mol of ethylene oxide, such as 2-methyl-branched C_{9-11} alcohols having on average 3.5 mol of ethylene oxide (EO) or C_{12-18} fatty alcohols having 1 to 4 EO, are also suitable. Owing to their high foaming characteristics they are used in cleaning agents in only relatively small amounts, for example in amounts from 1 wt.% to 5 wt.%.

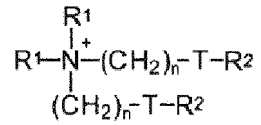
[0046] Further suitable anionic surfactants are also the salts of alkyl sulfosuccinic acid, which are also known as sulfosuccinates or sulfosuccinic acid esters, and the monoesters and/or diesters of sulfosuccinic acid with alcohols, preferably fatty alcohols and in particular ethoxylated fatty alcohols. Preferred sulfosuccinates contain C_{8-18} fatty alcohol residues or mixtures thereof. Sulfosuccinates that are preferred in particular contain a fatty alcohol residue derived from ethoxylated fatty alcohols which are non-ionic surfactants in their own right. In turn, sulfosuccinates whose fatty alcohol residues derive from ethoxylated fatty alcohols having a narrow homolog distribution are more preferred. It is likewise also possible to use alk(en)yl succinic acid having preferably 8 to 18 carbon atoms in the alk(en)yl chain or salts thereof.

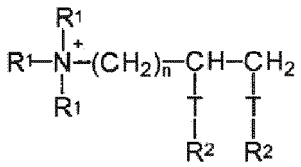
[0047] Further suitable anionic surfactants are in particular soaps. Saturated fatty acid soaps are suitable, such as the salts of lauric acid, myristic acid, palmitic acid, stearic acid, hydrogenated erucic acid and docosanoic acid, and in particular soap mixtures derived from natural fatty acids, for example coconut, palm kernel or tallow fatty acids.

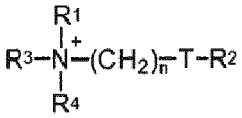
[0048] The anionic surfactants including the soaps can be present in the form of their sodium, potassium or ammonium salts and as soluble salts of organic bases, such as mono-, di- or triethanolamine. The anionic surfactants are preferably in the form of their sodium or potassium salts, in particular in the form of their sodium salts.

[0049] Cationic and/or amphoteric surfactants can also be used in place of or in conjunction with the specified surfactants.

[0050] For example, cationic compounds of the following formulae can be used as cationic active substances:







in which each R^1 group is selected independently of one another from C_{1-6} alkyl, alkenyl or hydroxyalkyl groups, each R^2 group is selected independently of one another from C_{8-28} alkyl or alkenyl groups; $R^3 = R^1$ or $(CH_2)_n$-T-R^2; $R^4 = R^1$ or R^2 or $(CH_2)_n$-T-R^2; T = -CH_2-, -O-CO- or -CO-O- and n is a whole number from 0 to 5.

[0051] Textile-softening compounds can be used to care for the textiles and to improve textile properties such as a softer "touch" (finishing) and reduced electrostatic charge (increased wear comfort). The active ingredients of these formulations are quaternary ammonium compounds having two hydrophobic residues, such as for example distearyl dimethyl ammonium chloride, which, however, because of its unsatisfactory biodegradability is increasingly being replaced by quaternary ammonium compounds containing in their hydrophobic residues ester groups as predetermined breaking points for biodegradation.

[0052] Such esterquats having improved biodegradability are obtainable for example by esterifying mixtures of methyl diethanolamine and/or triethanolamine with fatty acids and then quaternizing the reaction products in a manner known per se with alkylating agents. Dimethylol ethylene urea is also suitable as a finishing agent.

[0053] Enzymes can be used to increase the washing or cleaning performance of washing or cleaning agents. These include in particular proteases, amylases, lipases, hemicellulases, cellulases, perhydrolases or oxidoreductases, and preferably mixtures thereof. These enzymes are of natural origin in principle; starting from the natural molecules, improved variants are available for use in washing and cleaning agents which accordingly are preferably used. Washing or cleaning agents preferably contain enzymes in total amounts of 1 x 10^6 wt.% to 5 wt.%, relative to active protein. The protein concentration can be determined with the aid of known methods, for example the BCA method or the Biuret method.

[0054] Of the proteases, those of the subtilisin type are preferred. Examples thereof are the subtilisins BPN' and Carlsberg and the developed forms thereof, the protease PB92, the subtilisins 147 and 309, the alkaline protease from Bacillus lentus, subtilisin DY, and the enzymes thermitase, proteinase K and the proteases TW3 and TW7, which can be assigned to the subtilases but no longer in the narrower sense to the subtilisins.

[0055] Examples of amylases which can be used according to the invention are the α-amylases from Bacillus licheniformis, from B. amyloliquefaciens, from B. stearothermophilus, from Aspergillus niger and A. oryzae, and the further developments of the aforementioned amylases improved for use in washing and cleaning agents. Furthermore, the α-amylase from Bacillus sp. A 7-7 (DSM 12368) and the cyclodextrin glucanotransferase (CGTase) from B. agaradherens (DSM 9948) can be mentioned for this purpose.

[0056] Lipases or cutinases can be used because of their triglyceride-cleaving activity. These include for example the lipases obtainable originally from Humicola lanuginosa (Thermomyces lanuginosus) or the further developments thereof, in particular those with the amino acid exchange D96L. Furthermore, the cutinases that were originally isolated from Fusarium solani pisi and Humicola insolens can also be used, for example. Lipases or cutinases whose starting enzymes were originally isolated from Pseudomonas mendocina and Fusarium solanii can also be used.

[0057] Enzymes which are grouped together under the term hemicellulases can moreover be used. They include for example mannanases, xanthan lyases, pectin lyases (=pectinases), pectinesterases, pectate lyases, xyloglucanases (=xylanases), pullulanases and ß-glucanases.

[0058] To increase the bleaching action, oxidoreductases, for example oxidases, oxygenases, catalases, peroxidases, such as halo-, chloro-, bromo-, lignin, glucose or manganese peroxidases, dioxygenases or laccases (phenoloxidases, polyphenoloxidases) can be used if desired. Preferably organic, more preferably aromatic compounds which interact with the enzymes are advantageously additionally added to strengthen the activity of the oxidoreductases concerned

(enhancers) or to ensure the flow of electrons in the case of very differing redox potentials between the oxidizing enzymes and the stains (mediators).

[0059] The enzymes can be used in any form established according to the prior art. These include for example the solid preparations obtained by granulation, extrusion or lyophilization or, particularly in the case of agents in liquid or gel form, solutions of the enzymes, advantageously as concentrated as possible, with a low water content and/or mixed with stabilizers. For both the solid and the liquid presentation form, the enzymes can alternatively be encapsulated, for example by spray drying or extrusion of the enzyme solution together with a preferably natural polymer, or in the form of capsules, for example those in which the enzymes are enclosed as in a solidified gel or in those of the core-shell type, in which an enzyme-containing core is coated with a protective layer which is impermeable to water, air and/or chemicals. Further active ingredients, for example stabilizers, emulsifiers, pigments, bleaches or dyes, can additionally be applied in superimposed layers. Such capsules are applied by methods known per se, for example by vibrating or roll granulation or in fluidized-bed processes. Such granules are advantageously low in dust, for example through the application of polymeric film formers, and stable in storage because of the coating. It is also possible to make up two or more enzymes together so that a single granulated product has multiple enzyme activities.

[0060] One or more enzymes and/or enzyme preparations, preferably solid protease preparations and/or amylase preparations, are preferably used in amounts from 0.1 wt.% to 5 wt.%, preferably from 0.2 wt.% to 4.5 wt.% and in particular from 0.4 wt.% to 4 wt.%.

[0061] Individual fragrance compounds, for example synthetic products of the ester, ether, aldehyde, ketone, alcohol and hydrocarbon type, can be used as perfume oils or scents. Mixtures of different fragrances which together generate an attractive scent note are preferably used, however. Such perfume oils can also contain natural fragrance mixtures, such as are obtainable from plant sources, for example pine, citrus, jasmine, patchouli, rose or ylang-ylang oil. In order to be perceptible, a fragrance must be volatile, wherein in addition to the nature of the functional groups and the structure of the chemical compound, the molar mass also plays an important role. Thus, most fragrances have molar masses of up to approx. 200 g/mol, whereas molar masses of 300 g/mol and above constitute an exception. Owing to the differing volatility of fragrances, the odor of a perfume or scent composed of a plurality of fragrances changes as it evaporates, wherein the odor impressions are divided into "top note", "middle note" or "body", and "end note" or "dry-out". As the odor perception is also based to a great extent on the odor intensity, the top note of a perfume or scent does not consist solely of highly volatile compounds, whereas the end note consists largely of less volatile, i.e. fixative, fragrances. When composing perfumes, more highly volatile fragrances can be bound for example to certain fixatives, thus preventing their too rapid evaporation. Thus, the following categorization of fragrances into "more highly volatile" or "fixative" fragrances says nothing about the odor impression or whether the corresponding fragrance is perceived as a top note or middle note. The scents can be processed directly, but it can also be advantageous to apply the scents to carriers, which through a slower release of the scent ensure a long-lasting scent. Cyclodextrins for example have proved effective as such carrier materials, wherein the cyclodextrin perfume complexes can also additionally be layered with further auxiliary agents.

[0062] In choosing the coloring agent it is important to ensure that the coloring agents can have a high storage stability and photostability and not too strong an affinity to textile surfaces and in particular to synthetic fibers. At the same time it must also be borne in mind that coloring agents can exhibit differing levels of oxidation stability. Generally speaking, non-water-soluble coloring agents have a greater oxidation stability than water-soluble coloring agents. The concentration of the coloring agent in the washing or cleaning agents varies, depending on the solubility and hence also on the oxidation sensitivity. In the case of readily water-soluble coloring agents, coloring agent concentrations in the range from a few 10^{-2} wt.% to 10^{-3} wt.% are typically chosen. By contrast, in the case of pigment dyes which are preferred in particular because of their brilliance but which are less readily water-soluble, the suitable concentration of the coloring agent in washing or cleaning agents is typically a few 10^{-3} wt.% to 10^{4} wt.%. Coloring agents which can be broken down by oxidation in the washing process and mixtures thereof with suitable blue dyes known as blue toners are preferred. It has proved advantageous to use coloring agents that are soluble in water or at room temperature in liquid organic substances. For example, anionic coloring agents, e.g. anionic nitroso dyes, are suitable.

[0063] In addition to the hitherto cited components, the washing or cleaning agents can contain further ingredients which further improve the applicational and/or aesthetic properties of said agents. Preferred agents contain one or more substances from the group of electrolytes, pH adjusters, fluorescent agents, hydrotropes, foam inhibitors, silicone oils, anti-redeposition agents, optical brighteners, graying inhibitors, anti-shrink agents, anti-crease agents, dye transfer inhibitors, antimicrobial active ingredients, germicides, fungicides, antioxidants, antistatics, ironing aids, phobing and impregnating agents, non-swelling and anti-slip agents and UV absorbers.

[0064] A large number of the most diverse salts can be used as electrolytes from the group of inorganic salts. Preferred cations are the alkali and alkaline-earth metals, while preferred anions are the halides and sulfates. From a manufacturing perspective the use of NaCl or $MgCl_2$ in the washing or cleaning agents is preferred.

[0065] The use of pH adjusters can be indicated in order to bring the pH of washing or cleaning agents into the desired range. All known acids or bases can be used here, provided that their use is not prohibited on applicational or ecological

grounds or for reasons of consumer protection. The amount of these adjusters does not usually exceed 1 wt.% of the total formulation.

[0066] Soaps, oils, fats, paraffins or silicone oils, which can optionally be applied to carrier materials, are suitable as foam inhibitors. Inorganic salts such as carbonates or sulfates, cellulose derivatives or silicates and mixtures of the aforementioned materials, for example, are suitable as carrier materials. In the context of the present application preferred agents contain paraffins, preferably unbranched paraffins (n-paraffins) and/or silicones, preferably linear-polymer silicones, which are structured in accordance with the scheme $(R_2SiO)_x$ and are also known as silicone oils. These silicone oils are usually clear, colorless, neutral, odor-free, hydrophobic liquids having a molecular weight of between 1000 g/mol and 150,000 g/mol and viscosities of between 10 mPa·s and 1,000,000 mPa·s.

[0067] Suitable anti-redeposition agents are for example non-ionic cellulose ethers such as methyl cellulose and methyl hydroxypropyl cellulose having a methoxy group content of 15 to 30 wt.% and a hydroxypropyl group content of 1 to 15 wt.%, relative in each case to the non-ionic cellulose ethers.

[0068] The polymers of phthalic acid and/or terephthalic acid and derivatives thereof, in particular polymers of ethylene terephthalate and/or polyethylene glycol terephthalate, or anionically and/or non-ionically modified derivatives thereof, known from the prior art are suitable as soil repellents. Of those, the sulfonated derivatives of phthalic acid and terephthalic acid polymers are preferred in particular.

[0069] Optical brighteners can be added to washing agents in particular to eliminate graying and yellowing of the treated textiles. These substances attach to the fibers and bring about a brightening and simulated bleaching effect by converting invisible ultraviolet radiation into visible light of a longer wavelength, wherein the ultraviolet light absorbed from sunlight is radiated as a weakly bluish fluorescence and forms pure white with the yellow tone of grayed or yellowed laundry. Suitable compounds are derived for example from the substance classes of 4,4'-diamino-2,2'-stilbene disulfonic acids (flavonic acids), 4,4'-distyryl biphenylene, methylumbelliferones, coumarins, dihydroquinolinones, 1,3-diaryl pyrazolines, naphthalic acid imides, benzoxazole, benzisoxazole and benzimidazole systems and the pyrene derivatives substituted by heterocyclic compounds.

[0070] The role of graying inhibitors is to hold the dirt released by the fibers suspended in the liquor and thus to prevent the dirt from reattaching. Water-soluble colloids, mostly of an organic nature, are suitable for this purpose, for example the water-soluble salts of polymeric carboxylic acids, glue, gelatin, salts of ether sulfonic acids of starch or cellulose or salts of acid sulfuric acid esters of cellulose or starch. Water-soluble polyamides containing acid groups are also suitable for this purpose. Soluble starch preparations can moreover be used, for example degraded starch, aldehyde starches, etc. Polyvinylpyrrolidone can also be used. Furthermore, cellulose ethers such as carboxymethyl cellulose (Na salt), methyl cellulose, hydroxyalkyl cellulose and mixed ethers such as methyl hydroxyethyl cellulose, methyl hydroxypropyl cellulose, methyl carboxymethyl cellulose and mixtures thereof can be used as graying inhibitors.

[0071] As textile fabrics, in particular those made from rayon, spun rayon, cotton and mixtures thereof, can tend to crease, because the individual fibers are susceptible to being bent, buckled, pressed and crushed at right angles to the fiber direction, synthetic anti-crease agents can be used. These include for example synthetic products based on fatty acids, fatty acid esters, fatty acid amides, fatty alkylol esters, fatty alkylol amides or fatty alcohols, which are mostly reacted with ethylene oxide, or products based on lecithin or modified phosphoric acid esters.

[0072] Phobing and impregnating methods serve to treat textiles with substances which prevent dirt from being deposited or make it easier to wash out. Preferred phobing and impregnating agents are perfluorinated fatty acids, also in the form of the aluminum and zirconium salts thereof, organic silicates, silicones, polyacrylic acid esters with a perfluorinated alcohol component or polymerizable compounds coupled with a perfluorinated acyl or sulfonyl residue. Antistatics can also be included. The dirt-repellent treatment with phobing and impregnating agents is often classed as an easy-care treatment. The penetration of the impregnating agents in the form of solutions or emulsions of the corresponding active ingredients can be facilitated by adding wetting agents, which reduce the surface tension. A further area of use of phobing and impregnating agents is the water-repellent treatment of textile goods, tents, tarpaulins, leather, etc., in which, in contrast to waterproofing, the fabric pores are not closed and so the material remains breathable (hydrophobing). The hydrophobing agents used for hydrophobing coat textiles, leather, paper, wood, etc. with a very thin layer of hydrophobic groups, such as relatively long alkyl chains or siloxane groups. Suitable hydrophobing agents are for example paraffins, waxes, metal soaps, etc., with additions of aluminum or zirconium salts, quaternary ammonium compounds having long-chain alkyl residues, urea derivatives, fatty acid-modified melamine resins, chromium complex salts, silicones, organotin compounds and glutardialdehyde as well as perfluorinated compounds. The hydrophobed materials do not feel greasy, but - as on greased materials - water droplets roll off them without wetting them. Thus silicone-impregnated textiles for example have a soft feel and are water- and dirt-repellent; marks from ink, wine, fruit juices and the like are easier to remove.

[0073] Antimicrobial active ingredients can be used to combat microorganisms. A distinction is made here between bacteriostatics and bactericides, fungistatics and fungicides, etc., depending on the antimicrobial spectrum and mechanism of action. Substances from these groups are, for example, benzalkonium chlorides, alkylaryl sulfonates, halogen phenols and phenol mercuriacetate, wherein these compounds can also be dispensed with entirely.

[0074] The agents can contain antioxidants to prevent undesirable changes to the washing and cleaning agents and/or to the treated textiles caused by exposure to atmospheric oxygen and by other oxidative processes. This class of compounds includes for example substituted phenols, hydroquinones, catechols and aromatic amines as well as organic sulfides, polysulfides, dithiocarbamates, phosphites and phosphonates.

[0075] An increased wear comfort can result from the additional use of antistatics. Antistatics increase the surface conductivity and thus allow an improved discharge of charges that are formed. External antistatics are generally substances having at least one hydrophilic molecule ligand and they form a more or less hygroscopic film on the surfaces. These mostly interfacially active antistatics can be subdivided into nitrogen-containing (amines, amides, quaternary ammonium compounds), phosphorus-containing (phosphoric acid esters) and sulfur-containing (alkyl sulfonates, alkyl sulfates) antistatics. Lauryl (or stearyl) dimethyl benzyl ammonium chlorides are likewise suitable as antistatics for textiles or as an addition to washing agents, with a finishing effect additionally being achieved.

[0076] Silicone derivatives can be used in textile washing agents to improve the water absorbency and the rewettability of the treated textiles and to make it easier to iron the treated textiles. Through their foam-inhibiting properties they additionally improve the rinsing behavior of washing or cleaning agents. Preferred silicone derivatives are for example polydialkyl or alkylaryl siloxanes in which the alkyl groups have one to five C atoms and are wholly or partially fluorinated. Preferred silicones are polydimethyl siloxanes, which can optionally be derivatized and are then amino-functional or quaternized or which have Si-OH, Si-H and/or Si-Cl bonds. Further preferred silicones are the polyalkylene oxide-modified polysiloxanes, in other words polysiloxanes, which for example contain polyethylene glycols, and the polyalkylene oxide-modified dimethyl polysiloxanes.

[0077] Finally, UV absorbers, which attach to the treated textiles and improve the light resistance of the fibers, can also be used. Compounds having these desired properties are for example the compounds and derivatives of benzophenone having substituents in the 2- and/or 4-position which act by non-radiative deactivation. Furthermore, substituted benzotriazoles, acrylates substituted with phenyl in the 3-position (cinnamic acid derivatives), optionally having cyano groups in the 2-position, salicylates, organic Ni complexes and natural substances such as umbelliferone and urocanic acid, which is produced naturally in the body, are also suitable.

[0078] Owing to their fiber-conditioning action, protein hydrolysates are further suitable active substances. Protein hydrolysates are mixtures of products which are obtained by acidically, basically or enzymatically catalyzed breakdown of proteins. Protein hydrolysates of both plant and animal origin can be used. Animal protein hydrolysates are for example elastin, collagen, keratin, silk and milk protein hydrolysates, which can also be present in the form of salts. The use of protein hydrolysates of plant origin, for example soy, almond, rice, pea, potato and wheat protein hydrolysates, is preferred. Although the use of protein hydrolysates as such is preferred, amino acid mixtures obtained by other means or individual amino acids such as for example arginine, lysine, histidine or pyroglutamic acid can optionally be used in their place. The use of derivatives of protein hydrolysates, for example in the form of their fatty acid condensation products, is likewise possible.

Examples

Comparative Example 1: Synthesis of Polymer A

[0079] A mixture of 12.138 g (0.0892 mol) of Dimethylvinylphosphonate (DMVP) and 0.9095 g (2,38 mmol) of BlocBuilder® ((2-[N-tert-butyl-N-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminooxy]isobutyric acid; available from Arkema) was bubbled with argon for 30 mins to be then heated at 120°C for 3h under magnetic stirring. Conversion of DMVP (74%) was determined from ^{1}H NMR of the crude product. The latter product was precipitated in a mixture of cold pentane/tetrahydrofurane (THF) (50/50 in volume). 7.55 g of pure homopolymer was collected after drying at 40°C under reduced pressure. ^{1}H NMR performed on the precipitated product confirmed its chemical structure.

[0080] 6.66 g of the precipitated polymer ($M_{n,theo}$= 4173 g.mol-1, DP_n=27, moles of ester groups=0.0862) was dissolved in 42.518 g (0.431 moles) of concentrated HCl (37%, molar excess of 5 with respect to ester groups). The medium was heated under reflux for 12 h. The resulting crude product was heated under reduced pressure at 80°C to remove water and excess HCl. The product was then washed with THF and next with pentane. 5.02 g of polymer was collected after drying at 40°C under reduced pressure. ^{1}H NMR before and after hydrolysis showed total disappearance of protons corresponding to dimethyl ester groups. The calculated theoretical molecular weight amounts to 3010 g.mol^{-1}.

Example 2: Synthesis of Polymer B

Prior synthesis of S-(4-vinylbenzyl) S'-propyltrithiocarbonate (VBPT):

[0081] To 30.00 g (0.394 mol) of 1-propanethiol in 320 ml of anhydrous methanol, under an argon flux, was slowly added a solution of 21.49 g (0.398 mol) of sodium methoxide dissolved in 373 ml of anhydrous methanol. After 2h, 37.49

g (0.492 mol) of carbon disulfide was added dropwise and the resulting mixture was allowed to stir at room temperature for 5 h. A yellow solution was observed. To this solution, 65.83 g (0.431 mol) of 4-vinylbenzyl chloride was slowly added and the mixture was left to stir overnight under argon. 200 ml of water was added to mixture and the latter was washed three times with dichloromethane The organic phases were gathered, washed with a saturated solution of NaCl, dried over $MgSO_4$, filtered and finally vacuum dried to remove the extraction solvent. The crude product was purified by silica gel column chromatography with heptane as the eluant. 110 g of yellow viscous oil of VBPT were recovered with a yield of 93 %.

Step 1: Synthesis of hyper P(DMVP)

[0082] 50.846 g (0.374 mol) of dimethylvinylphosphonate (DMVP), 2.236 g (8.33 mmol) of VBPT and 0.4040 g (0.644 mol) of AIBN were dissolved in 106 ml of DMSO. The medium was bubbled with argon for 30 mins, after which a temperature of 70°C was applied for 22h. Conversions of DMVP and VBPT were determined from ^{1}H NMR from the crude product. The latter was then precipitated in cold pentane/THF (50/50 vol/vol). After solvent removal under vacuum at a temperature of 40°C, ^{1}H NMR and UV-vis were performed on the precipitated hyper.P(DMVP) to verify the chemical structure and the presence of thiocarbonate groups respectively. 26.85 g DMVP-based hyberbranched copolymer (hyper.P(DMVP)) was obtained.

Step 2 Aminolysis of hyper.P(DMVP)

[0083] 7,995 g (2.48 mmol of trithiocarbonate) of hyper.P(DMVP) and 3.2570 g (0.0124 mol) of triphenylphosphine (PPh_3) were dissolved in 21 mL of DMF. 1.2819 g (0.0127 mol) of hexylamine was then added. The medium was left under magnetic stirring for 5 h at room temperature. The crude product was then precipitated in cold diethyl ether. ^{1}H NMR and UV-vis were performed on the resulting precipitated aminolysed hyper.P(DMVP) to verify the chemical structure and attest the absence of thiocarbonate groups after aminolysis.

Step 3 Michael addition of aminolysed hyper.P(DMVP) and PEG:

[0084] 6.500 g of the aminolysed hyper.P(DMVP) from step 2 bearing 2.02 mmol of thiol groups and 2.644 g (0.0101 mol) of PPh_3 were dissolved in 16 ml of DMF. 1.020 g (0.0101 mol) of triethylamine and 9.678 g (0.0202 mol) of PEG methyl ether acrylate (M_n=480 g·mol^{-1}) were successively added. The medium was left under magnetic stirring for 24 h at room temperature. The crude product was then precipitated on cold diethyl ether. ^{1}H NMR was carried out on the precipitated aminolysed hyperbranched P(DMVP) decorated with PEG (hyper.P(DMVP)$_{PEG}$).

Step 4: Hydrolysis of hyper.P(DMVP) decorated with PEG

[0085] 7.000 g of the hyperbranched polymer hyper.P(DMVP)$_{PEG}$ from step 4 containing 0.051 mol of dimethyl ester groups was dissolved in 70 ml of dichloromethane. 28.16 g (0.184 mol) of trimethylsilylbromide (TMSBr) was added. The medium was stirred for 3 h at room temperature. The reaction mixture was then concentrated under reduced pressure. 100 ml of methanol was added and the mixture was stirred for 5h to be eventually concentrated under vacuum. The resulting product was washed with THF, then pentane and was ultimately vacuum dried at 40°C. ^{1}H NMR was carried out on the hydrolyzed hyperbranched VPA-based polymer decorated with PEG (hyper.P(VPA)$_{PEG}$; Polymer B) to confirm its structure.

Example 3: Synthesis of Polymer C

Step 1: RAFT copolymerization of VBPT AND DMVP

[0086] 5.034 g (0.0188 mol) of VBPT, 39.990 g (0.294 mol) of DMVP and 0.9181 g (5.59 mmol) of AIBN were dissolved in 88 ml of DMSO. The medium was bubbled with argon for 30 mins, after which a temperature of 70°C was applied for 22 h. Conversions of DMVP (62%) and VBPT (100%) were determined from ^{1}H NMR from the crude product. The latter was then precipitated in cold diethyl ether. After solvent removal under vacuum at a temperature of 40°C, ^{1}H NMR and UV-vis were performed on the precipitated hyper.P(DMVP) to verify the chemical structure and the presence of thiocarbonate groups respectively. 30 g DMVP-based hyberbranched copolymer (hyper.P(DMVP)) were obtained.

Step 2: Aminolysis of hyper.P(DMVP)

[0087] 10 g (6.25 mmol of trithiocarbonate) of hyper.P(DMVP) and 8.197 g (0.0313 mol) of PPh_3 were dissolved in 20

ml of DMF. 3.163 g (0.0313 mol) of hexylamine was then added. The medium was left under magnetic stirring for 5 h at room temperature. The crude product was then precipitated in cold diethyl ether. ^{1}H NMR and UV-vis were performed on the resulting precipitated aminolysed hyper.P(DMVP) to verify the chemical structure and attest the absence of thiocarbonate groups after aminolysis.

Step 3: Michael addition of aminolysed hyper.P(DMVP) and PEG

[0088] The aminolysed hyper.P(DMVP) from step 2 bearing 6.25 mmol of thiol groups and 8.197 g (0.0313 mol) of PPh_3 were dissolved in 100 ml of DMF. 3.162 g (0.0313 mol) of triethylamine and 30 g (0.0625 mol) of PEG methyl ether acrylate (M_n=480 g·mol^{-1}) were successively added. The medium was left under magnetic stirring for 24 h at room temperature. The crude product was then precipitated on cold diethyl ether. ^{1}H NMR was carried out on the precipitated aminolysed hyperbranched P(DMVP) decorated with PEG (hyper.P(DMVP)$_{PEG}$) for chemical structure confirmation.

Step 4: Hydrolysis of hyper.P(DMVP) decorated with PEG

[0089] The hyperbranched polymer hyper.P(DMVP)$_{PEG}$ from step 4 containing 0.119 mol of dimethyl ester groups was dissolved in 100 ml of dichloromethane. 32.7 g (0.214 mol) of TMSBr was added. The medium was stirred for 3 h at room temperature. The reaction mixture was then concentrated under reduced pressure. 100 ml of methanol was then added and the mixture was stirred for 5h to be next concentrated under vacuum. The resulting product was washed with THF, then pentane and was ultimately vacuum dried at 40°C. ^{1}H NMR of the precipitated product confirmed the right structure. 6.13 g of hyper.P(VPA)$_{PEG}$, Polymer C, were gathered.

Example 4: Cleaning performance

[0090] Miniaturized washing tests were performed in triplicate at 40°C on standardized tea stains on cotton fabric. A bleach-free aqueous liquid detergent (LWA) and liquid detergents otherwise identical to LWA, but containing 2 wt.% of the polymers produced in examples 1 to 3 and 2 wt.% less of water, were used for the washing tests (concentration of detergent 4.1 g/l; duration 60 minutes). The tests were evaluated by measuring the color difference according to the L*a*b* values and the resulting Y values as a measure of the brightness. The table below shows the ddY-values, that is the differences between dY values for LWA and for LWA + polymer, dY being the difference between Y(after washing) and Y(before washing).

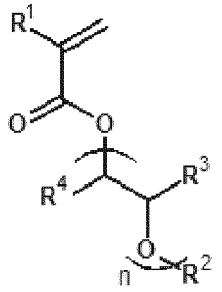
Table 1: ddY-values

LWA + polymer A	LWA + polymer B	LWA + polymer C
3.43	7.81	9.83

[0091] As can be seen, the values obtained with the detergents comprising the polymers according to invention (polymers B and C) are greater than those obtained using only the liquid detergent, but also than those obtained by the detergent comprising the comparative polymer A; this corresponds to a higher degree of whiteness and hence to an improved stain removal.

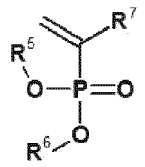
Claims

1. Use of copolymers, obtainable by radical-induced copolymerization of monomers according to formula I,



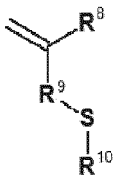
(I)

in which, independently from each other, R^1 and R^2 is H or an alkyl group with 1 to 4 C-atoms, R^3 and R^4 is H or a methyl group, and n is a number from 1 to 200, with
monomers according to formula II,



(II)

in which, independently from each other, R^5, R^6 and R^7 is H or an alkyl group with 1 to 4 C-atoms with the proviso that at least one of R^5 and R^6 is H, and with
branching monomers according to formula III,



(III)

in which

R^8 is H or or an alkyl group with 1 to 4 C-atoms,
R^9 is -C(O)-O-R^{11}-, -C(O)-N$R^{11}R^{12}$-, -O-R^{11}-, an arylene group, a linear or branched alkylene group with 1 to 20 C-atoms, or -$(CH_2$-CHR^{13}-$O)_m$-,
R^{10} is -C(S)-S-R^{14}, -C(S)-R^{15}, -C(S)-N$R_{16}R_{17}$ or -C(S)-O-R^{18}
R^{11} is a linear or branched alkylene group with 1 to 20 C-atoms, or -$(CH_2$-CHR^{13}-$O)_m$-,
R^{12} is H or a linear or branched alkylene group with 1 to 20 C-atoms, or -$(CH_2$-CHR^{13}-$O)_m$-,
R^{13} is H or a methyl group,
R^{14} is a linear or branched alkylene group with 1 to 20 C-atoms, or a pyrrolidone group,
R^{15} is an aryl group or a linear or branched alkylene group with 1 to 20 C-atoms, or a pyrrolidone group,
R^{16}, R^{17} and R^{18} are, independently from each other, H, an aryl group, a linear or branched alkyl group with 1 to 20 C-atoms, or, -$(CH_2$-CHR^{13}-$O)_m$-H, and
m is a number of from 1 to 20 in washing and cleaning detergents to improve the cleaning performance, especially with respect to bleach-sensitive stains.

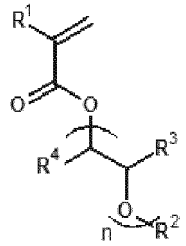
2. Use according to claim 1, **characterized in that** the improved cleaning performance consists in an improved removal of stains containing polymerizable substances, in particular polymerizable dyes.

3. Use according to claim 2, **characterized in that** the polymerizable substances are selected from polyphenolic dyes, in particular from flavonoids, above all from dyes of the class of anthocyanidins or anthocyanins or oligomers of said compounds.

4. Use according to any of claims 1 to 3, **characterized in that** the improved cleaning performance consists in an improved removal of red- to blue-colored stains, in particular of red wine marks or marks from fruit or vegetables containing red- to blue-colored dyes, or from drinks or food products containing such fruit or vegetables.

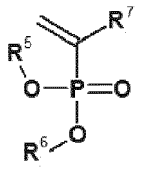
5. Use according to any of claims 1 to 4, **characterized in that** the stains are selected from stains from cherries, red grapes, pomegranate, chokeberry, plums, sea buckthorn, acai, berries, in particular redcurrants or blackcurrants, elderberries, blackberries, raspberries, blueberries, lingonberries, cowberries, strawberries or bilberries, red cabbage, blood orange, eggplant, black carrot, red- or blue-fleshed potatoes or red onions.

6. A washing or cleaning detergent **characterized in that** it contains a copolymer, obtainable by radical-induced copolymerization of monomers according to formula I,



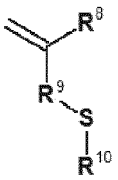
(I)

in which, independently from each other, R^1 and R^2 is H or an alkyl group with 1 to 4 C-atoms, R^3 and R^4 is H or a methyl group, and n is a number from 1 to 200, with
monomers according to formula II,



(II)

in which, independently from each other, R^5, R^6 and R^7 is H or an alkyl group with 1 to 4 C-atoms with the proviso that at least one of R^5 and R^6 is H, and with
branching monomers according to formula III,



(III)

in which

R^8 is H or or an alkyl group with 1 to 4 C-atoms,
R^9 is -C(O)-O-R^{11}-, -C(O)-N$R^{11}R^{12}$-, -O-R^{11}-, an arylene group, a linear or branched alkylene group with 1 to 20 C-atoms, or -$(CH_2$-CHR^{13}-$O)_m$-,
R^{10} is -C(S)-S-R^{14}, -C(S)-R^{15}, -C(S)-N$R_{16}R_{17}$, or -C(S)-O-R^{18}
R^{11} is a linear or branched alkylene group with 1 to 20 C-atoms, or -$(CH_2$-CHR^{13}-$O)_m$-,
R^{12} is H or a linear or branched alkylene group with 1 to 20 C-atoms, or -$(CH_2$-CHR^{13}-$O)_m$-,
R^{13} is H or a methyl group,
R^{14} is a linear or branched alkylene group with 1 to 20 C-atoms, or a pyrrolidone group,
R^{15} is an aryl group or a linear or branched alkylene group with 1 to 20 C-atoms, or a pyrrolidone group,
R^{16}, R^{17} and R^{18} are, independently from each other, H, an aryl group, a linear or branched alkyl group with 1 to 20 C-atoms, or, -$(CH_2$-CHR^{13}-$O)_m$-H, and
m is a number of from 1 to 20.

7. Detergent according to claim 6, **characterized in that** it contains 0.01 wt.% to 5 wt.%, in particular 0.1 wt.% to 2 wt.% of the polymer.

8. Detergent according to claim 6 or 7, **characterized in that** it contains no bleaching agents.

9. Use according to any of claims 1 to 5 or detergent according to any of claims 6 to 8, **characterized in that** in formula I R^1, R^2, R^3 and R^4, independently form each other, are H or methyl groups, wherein, in particular, R^3 and R^4 are not both methyl groups; and/or that n is a number from 1 to 50; and/or that in the monomers according to formula II both R^5 and R^6 are H, and/or R^7 is H.

10. Use or detergent to any prior claim, **characterized in that** the copolymers have average molar masses in the range from 1000 g/mol to 500,000 g/mol, in particular from 1000 g/mol to 250,000 g/mol, and/or they comprise units

stemming from monomers according to formula II and units stemming from monomers according to formula III in molar ratios in the range of from 1:1 to 100:1, in particular from 10:1 to 50:1.

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EUROPEAN SEARCH REPORT

Application Number
EP 18 18 5929

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 2006/131195 A1 (HENKEL KGAA [DE]) 14 December 2006 (2006-12-14) * page 4, paragraph 3 - page 5, paragraph 1 * * example * * claims *	1,5-10	INV. C11D3/37
X	GB 1 290 724 A (HOECHST AG [DE]) 27 September 1972 (1972-09-27) * page 1, lines 13-35 * * page 2, lines 11-26 * * examples * * claims *	1,2,5-10	
A	WO 2011/023717 A1 (HENKEL AG & CO KGAA [DE]) 3 March 2011 (2011-03-03) * page 1, paragraphs 3, 4 * * page 2, paragraphs 6, 7 * * page 9, paragraph 6 * * claims 1-9, 16, 18 *	1-10	
A	EP 0 877 076 A2 (ROHM & HAAS [US]) 11 November 1998 (1998-11-11) * page 2, line 26 - page 3, line 8 * * examples * * claims *	1-10	TECHNICAL FIELDS SEARCHED (IPC) C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	31 January 2019	Bertran Nadal, Josep

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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31-01-2019

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2006131195 A1	14-12-2006	AT 461992 T	15-04-2010
		DE 102005026522 A1	14-12-2006
		EP 1888733 A1	20-02-2008
		ES 2341674 T3	24-06-2010
		JP 5289050 B2	11-09-2013
		JP 2008542509 A	27-11-2008
		US 2008090746 A1	17-04-2008
		WO 2006131195 A1	14-12-2006
GB 1290724 A	27-09-1972	CH 509404 A	30-06-1971
		DE 1801411 A1	21-05-1970
		FR 2022230 A1	31-07-1970
		GB 1290724 A	27-09-1972
		SE 347525 B	07-08-1972
WO 2011023717 A1	03-03-2011	DE 102009028892 A1	03-03-2011
		EP 2470634 A1	04-07-2012
		US 2012157369 A1	21-06-2012
		WO 2011023717 A1	03-03-2011
EP 0877076 A2	11-11-1998	BR 9801607 A	18-05-1999
		CA 2236979 A1	09-11-1998
		CN 1199090 A	18-11-1998
		DE 69819593 T2	16-09-2004
		EP 0877076 A2	11-11-1998
		US 6489287 B1	03-12-2002

EPO FORM P0459

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