HIGHLY BRANCHED POLYMERS FOR WRINKLEPROOFING CELLULOSIC TEXTILES

Inventors: Jurgen Detering, Limburgerhof (DE); Peter Neumann, Mannheim (DE); Bernd Bruchmann, Freinsheim (DE)

Correspondence Address: OBLON, SPIVAK, MCCLELLAND, MAIER & NEUSTADT, P.C.
1940 DUKE STREET
ALEXANDRIA, VA 22314 (US)

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ABSTRACT
A process for wrinklespoofing cellulotic textiles by treating the textiles with a finish and drying the treated textiles, which comprises using a finish comprising one or more highly branched polymers in dissolved or dispersed form.
HIGHLY BRANCHED POLYMERS FOR WRINKLEPROOFING CELLULOSIC TEXTILES

[0001] This invention relates to processes for wrinklproofing cellulose textiles, wrinklproofing finishes comprising highly branched polymers, the use of the finishes and of the highly branched polymers, and also textile treatments, solid and liquid laundry detergents and laundry refreshers comprising highly branched 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 manufacture 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 compared with untreated cellulose textiles.

[0003] WO 92/01773 discloses the use of microemulsified aminosiloxanes in fabric conditioners to reduce wrinkling and creasing during the laundering process. In addition, the use of aminosiloxanes is said to facilitate ironing.

[0004] WO 98/4772 discloses a process for pretreating textile materials by applying a mixture of polycarboxylic acid and a cationic softener to the textile materials. Wrinkle control is obtained as a result.

[0005] EP-A 0 300 525 discloses fabric conditioners based on crosslinkable amino-functionalized silicones that impart wrinkle control or an easy-iron effect to textiles treated therewith.

[0006] WO 99/55953 discloses fabric wrinkle control compositions. They comprise lubricants, lithium salts and optionally further ingredients such as softeners, ionic and nonionic surfactants, odor control agents and bactericides. The formulation is preferably applied to the textile material by spraying.


[0008] It is an object of the present invention to provide a further process for wrinklproofing cellulose textiles and also further finishes for wrinklproofing such textiles.

[0009] We have found that this object is achieved by a process for wrinklproofing cellulose textiles by treating the textiles with a finish and drying the treated textiles, which comprises using a finish comprising one or more highly branched polymers in dissolved or dispersed form.

[0010] The invention also provides a wrinklproofing finish for cellulose textiles that comprises these highly branched polymers.

[0011] Highly branched polymers are known per se. Dendrimers, arborols, starburst polymers and hyperbranched polymers are designations for polymeric structures distinguished by a branched structure and a high functionality.

[0012] Dendrimers are molecularly and structurally uniform macromolecules having a highly symmetrical construction. They are constructed in multistage syntheses and are very costly as a result.

[0013] In contrast, hyperbranched polymers are both molecularly and structurally nonuniform. They have branches that differ in length and the degree of branching. The highly branched polymers used according to the invention are preferably such hyperbranched polymers in the narrower sense. But it is also possible to use structurally and molecularly uniform dendrimeric polymers. "Highly branched polymers" for the purposes of this invention therefore includes hyperbranched and dendrimeric polymers.

[0014] The highly branched polymers used according to the invention can be prepared in particular from AB₃ monomers. These have two different functional groups A and B which are capable of reacting with each other to form a linkage. There is only one functional group A per molecule, while B is present two or more times. The AB₃ monomers react with each other to form unbranched polymers having regularly disposed branching sites. There are almost exclusively B groups at the polymer chain ends. More particular details are described for example in J.M.S.—Rev. Macromol. Chem. Phys., C37(3), 555-579 (1997).

[0015] Highly branched polymers having functional groups may be synthesized in a principally known manner using AB₄, preferably AB₅, monomers. The AB₅ monomers may be completely incorporated in the form of branchings; they can be incorporated as terminal groups, i.e. still have two free B groups; or they can be incorporated as linear groups having a free B group. The highly branched polymers obtained have a certain number of B groups, either terminally or as side groups, depending on the degree of polymerization. Further particular concerns for hyperbranched polymers and their synthesis are to be found for example in J.M.S.—Rev. Macromol. Chem. Phys., C37(3), 555-579 (1997) and the references cited therein.

[0016] The choice of highly branched polymers for use in the wrinklproofing process of the invention is in principle not limited to a specific class of polymers. Useful polymers include highly branched polyesters, highly branched polyethers, highly branched polyurethanes, highly branched polyureas, highly branched polyamides, highly branched polysiloxanes, highly branched carbosilanes, highly branched polyetheramides and also highly branched polyesters. But highly branched polyurethanes, highly branched polyesters, highly branched polyethers, highly branched polyetheramides and highly branched polyamides are particularly useful. Among highly branched polyesters, it is specifically the highly branched polyethyleneimines which are suitable. Very particular preference is given to highly branched polyurethanes.

[0017] Highly branched polymers are preparable for example as follows:

[0018] Highly branched polyurethanes according to WO 97/02904 or according to DE 199 04 444

[0019] Highly branched polyesters according to SE 468771 or according to SE 503342

[0020] Highly branched polyesters according to DE 199 47 631

[0021] Highly branched polyetheramides according to WO 99/16810
Highly branched and highly functional polymers obtained by polymerization of AB₂ molecules may in principle be used as such in the finishes of the invention, provided the functional groups obtained in the train of the particular embodiment of the synthesis are suitable for application of the polymers in dissolved or dispersed form.

However, the B groups originally present may also be transfunctionalized by polymer-analogous reaction with suitable compounds.

Examples of suitable functional groups for introduction by means of suitable reaction partners include especially acidic or basic groups that contain H atoms and also derivatives thereof such as —COOH, —COOR, —CONHR, —CONH₂, —OH, —SH, —NH₂, —NHR, —NR₂, —NR₃, —SO₂H, —SO₂R, —NHOOR, —NHCOMH₂, —NHCONHR or salts thereof. The R radicals are generally straight-chain or branched alkyl radicals which may be further substituted, for example by C₃H₇-alkyl radicals. But other functional groups such as —CN or —OR, for example, may also be introduced.

In a preferred embodiment, the highly branched polymers used according to the invention contain one or more functional groups selected from the group consisting of —COOH, —COOR, —CONHR, —CONH₂, —OH, —SH, —NH₂, —NHR, —NR₂, —NR₃, —SO₂H, —SO₂R, —NHOOR, —NHCONHR or salts thereof.

The compounds used for transfunctionalization may contain not only the desired functional group but also a second group capable of reacting with the B groups of the highly branched polymer starting material to form a bond. An example is the reaction of an isocyanate group with a hydroxyxycarboxylic acid.

But it is also possible to use monofunctional compounds with which existing groups are merely modified. For example, alkyl halides may be used to quaternize existing amino groups.

The transfunctionalization of hyperbranched polymers may advantageously be carried out immediately following the polymerization reaction or in a separate reaction.

Functional groups having sufficiently acidic hydrogen atoms may be converted into the corresponding salts by treatment with suitable bases. Similarly, basic groups are convertible with suitable acids into the corresponding salts. This makes it possible to obtain highly branched polymers that are soluble in water.

It is also possible to generate highly branched polymers having different functionalities. This may be effectuated by reaction with a mixture of various compounds for transfunctionalization or else by reacting only a portion of the functional groups originally present.

The degree of polymerization, the molar mass and the type and number of functional groups are selectable by the skilled person according to the intended application.

Particularly preferred functional groups are —COOH, —CONH₂, —OH, —NH₂, —NHR, —NR₂, —NR₃ and —SO₂H and salts thereof.

In an advantageous embodiment, the highly branched polymers used according to the invention contain one or more functional groups selected from the group consisting of —COOH, —OH, —SO₂H and salts thereof.

In a further advantageous embodiment, the highly branched polymers used according to the invention contain one or more functional groups selected from the group consisting of —NH₂, —NHR, —NR₂, —NR₃ and salts thereof.

The highly branched polymers used according to the invention have on average at least 4 functional groups per molecule. The number of functional groups has in principle no upper limit. However, products having an excessively large number of functional groups frequently have undesirable properties, for example poor solubility or a very high viscosity. Therefore, the highly branched polymers used according to the invention preferably do not have more than 200 functional groups on average. Preferably the highly branched polymers have from 4 to 150, particularly preferably from 4 to 100, functional groups on average.

The molar masses of the highly branched polymers used according to the invention depend on the particular class of polymer and are chosen accordingly by one skilled in the art. Suitable products have a weight average molecular weight Mₐ of from 1 000 to 20 000 g/mol, preferably of from 1 000 to 100 000 g/mol.

Preferred highly branched polymers for use in the finishes of the invention are highly branched polyurethanes.

As used herein, the term "polyurethanes" extends beyond the customary understanding and includes polymers which are obtainable by reaction of di- or polyisocyanates with active-hydrogen compounds and which are linkable together by urethane structures, but also for example by urea, allophanate, biuret, carbodiimide, amide, uretonimine, uretidione, isocyanurate or oxazolidone structures.

The hyperbranched polyurethanes used according to the invention are preferably synthesized using AB₂ monomers containing not only isocyanate groups but also groups capable of reacting with isocyanate groups to form a linkage. x is a natural number between 2 and 8, preferably 2 or 3. Either A is an isocyanate group and B an isocyanate-reactive group, or vice versa.

Isocyanate-reactive groups are preferably OH, NH₂, NHR or SH groups.

AB₂ monomers are preferably synthesized for example by the method described in WO 97/02304 using protecting group techniques. This technique may be illustrated with reference to the preparation of an AB₂ monomer from 2,4-toluylene disocyanate (TDI) and trimethylolpropane. First, one of the isocyanate groups of the TDI is blocked in a conventional manner, for example by reaction with an oxide. The remaining free NCO group is reacted with trimethylolpropane, although only one of the three OH groups reacts with the isocyanate group, the other two OH groups being blocked via acetalization. Elimination of the protective group leaves a molecule having one isocyanate group and two OH groups.

A particularly advantageous way to synthesize AB₂ molecules is by the method described in DE-A 199 04 444,
where no protective groups are required. Di- or polysiocyanates are used in this method and reacted with compounds having at least two isocyanate-reactive groups. At least one of the reactants has groups having a reactivity that differs with regard to the other reactant. Preferably, both reactants have groups that differ in reactivity with regard to the other reactant. The reaction conditions are chosen in such a way that only certain reactive groups can react with each other.

0044] Useful di- and polysiocyanates include the aliphatic, cycloaliphatic and aromatic isocyanates known from the prior art. Preferred di- or polysiocyanates are 4,4'-diphenylmethane diisocyanate, the mixtures of monomeric diphenyl methane diisocyanates and oligomeric diphenylmethane diisocyanates (polymer MDI), tetramethylene diisocyanate, hexamethylene diisocyanate, 4,4'-methylenebis(cyclohexyl) diisocyanate, xylylene diisocyanate, tetramethylxylylene diisocyanate, dodecyl diisocyanate, lysine alkyl ester diisocyanate, where alkyl is C2-C10-alkyl, 2,2,4- or 2,4,4-trimethyl-1,6-hexamethylene diisocyanate, 1,4-diisocyanatocyclohexane or 4-isocyanatomethyl-1,8-octamethylethylenedioxycyanate.

0045] Particular preference is given to di- or polysiocyanates having NCO groups of different reactivities, such as 2,4-tolylenediisocyanate (2,4-TDI), 2,4-diphenylmethane diisocyanate (2,4-MDI), triisocyanatotoluene, isophorone diisocyanate (IPDI), 2-butyl-2-ethylpentamethylenedioxycyanate, 2-isocyanatopropylcyclohexyl isocyanate, 3(4)-isocyanatomethyl-1-methylcyclohexyl isocyanate, 1,4-diisocyanato-4-methylpentane, 2,4'-methylenebis(cyclohexyl) diisocyanate and 4-methylcyclohexane 1,3-diisocyanate (H-TDI). Particular preference is further given to isocyanates (b) whose NCO groups initially have equal reactivity, but where first addition of an alcohol or amine to an NCO group can be used to induce a reactivity reduction for the second NCO group. Examples thereof are isocyanates whose NCO groups are coupled via a delocalized electron system, for example 1,3- and 1,4-phenylene diisocyanate, 1,5-naphthylene diisocyanate, diphenyl diisocyanate, toluene diisocyanate or 2,6-tolylenediisocyanate.

0046] It is further possible to use for example oligo- or polysiocyanates preparable from the di- or polysiocyanates mentioned or mixtures thereof by linkage by means of urethane, allophanate, urca, isoniurate, carbodiimide, uretonimine, oxadiazinetrione or iminooxadiazinedione structures.

0047] Compounds used as having at least two isocyanate-reactive groups are preferably di-, tri- or tetrafuctional compounds whose functional groups have different reactivities toward NCO groups. Preference is given to compounds having at least one primary and at least one secondary hydroxyl group, at least one hydroxyl group and at least one mercapto group, particularly preferably having at least one hydroxyl group and at least one amino group in the molecule, especially amino alcohols, aminodiols and aminotriols, since amino is substantially more reactive with isocyanate than hydroxyl.

0048] Examples of compounds having at least two isocyanate-reactive groups are propylene glycol, glycerol, mercaptoethanol, ethanolamine, N-methylethanolamine, diethanolamine, ethanolpropanolamine, dipropanolamine, diisopropanolamine, 2-amino-1,3-propanediol, 2-amino-1,3-propanediol or tri(hydroxymethyl)aminomethane. Mixtures of the compounds mentioned may also be used.

0049] The preparation of an AB2 molecule may be illustrated for a diisocyanate with an aminodiol. First one mole of a diisocyanate is reacted with one mole of aminodiol at low temperatures, preferably in the range from 10 to 30°C. The urethane-forming reaction is virtually completely suppressed in this temperature range and the more reactive NCO groups of the isocyanate react exclusively with the amino group of the aminodiol. The AB2 molecule formed has one free NCO group and two free OH groups and can be used for synthesizing a highly branched polyurethane.

0050] On heating and/or catalyst addition this AB2 molecule can react intermolecularly to form a highly branched polyurethane. The synthesis of the highly branched polyurethane may advantageously be effected without prior isolation of the AB2 molecule in a further reaction step at elevated temperature, preferably in the range from 50 to 80°C. Using the above-described AB2 molecule having two OH groups and one NCO group provides a highly branched polymer having per molecule one free NCO group and also—depending on the degree of polymerization—a certain number of OH groups. The reaction can be carried on to high conversions to provide very high molecular weight structures. But it may also be discontinued for example by addition of suitable monofunctional compounds or by addition of one of the starting compounds for preparing the AB2 molecule on attainment of the desired molecular weight. Depending on the starting compound used for the termination, this provides either completely NCO-terminated or completely OH-terminated molecules.

0051] Alternatively, it is also possible for example to prepare an AB2 molecule from one mole of glycerol and 2 mol of 2,4-TDI. The primary alcohol groups and the isocyanate group in position 4 react preferentially at low temperature to form an adduct which has one OH group and two isocyanate groups and which, as described, can be converted at higher temperatures into a highly branched polyurethane. This initially provides a highly branched polymer which has one free OH group and—depending on the degree of polymerization—a certain number of NCO groups.

0052] The highly branched polyurethanethanes may in principle be prepared without solvent, but are preferably prepared in solution. Useful solvents include in principle all compounds that are liquid at room temperature and inert toward the monomers and polymers.

0053] Other products are obtainable through further synthetic variants. AB2 molecules are obtainable for example by reacting diisocyanates with compounds having at least 4 isocyanate-reactive groups. An example is the reaction of 2,4-tolylenediisocyanate with tri(hydroxymethyl)aminomethane.

0054] The polymerization may also be terminated using polyfunctional compounds capable of reacting with the respective A groups. This makes it possible to link a plurality of small highly branched molecules together to form a large highly branched molecule.

0055] Highly branched polymers having chain-extended branches are obtainable for example by using for the polymerization reaction as well as the AB2 molecules addition-
ally in a molar ratio of 1:1 a diisocyanate and a compound having two isocyanate-reactive groups. These additional AA or BB compounds may also have further functional groups which however must not be reactive toward the A or B groups under the reaction conditions chosen. This makes it possible to introduce further functionalities into the hyperbranched polymer.

[0056] Further synthetic variants for highly branched polyurethanes are disclosed in the applications DE 100 13 187.5 and DE 100 30 869.4.

[0057] The highly branched and highly functional polyurethanes obtained may be used as such in the finishes of the invention, provided the functional groups obtained in the course of the synthesis are suitable for use with the polyurethanes in dissolved or dispersed form.

[0058] But, as stated above, the functional groups may also be hydrophobicized, hydrophilicized or transfunctionnalized. This makes highly branched polyurethanes available that are particularly suitable for use as solution or aqueous dispersion. Owing to their reactivity, highly branched polyurethanes containing isocyanate groups are very particularly useful for transfunctionnalization. It is also possible to transfunctionnalize OH— or NH₂-terminated polyurethanes by means of suitable reaction partners.

[0059] Preferred groups for introduction into highly branched polyurethanes are —COOH, —CONH₂, —OH, —NH₂, —NHR, —NR₂, —NR₃⁺, —SO₃H and salts thereof. —NH₂, —NHR, —NR₂ and —NR₃⁺ are particularly preferred in one embodiment of the invention, and —COOH, —OH and —SO₃H in another embodiment of the invention.

[0060] Groups having sufficiently acidic hydrogen atoms are convertible into the corresponding salts by treatment with suitable bases. Similarly, basic groups are convertible into the corresponding salts using suitable acids. This makes it possible to obtain highly branched polyurethanes that are soluble in water.

[0061] By reacting NCO-terminated products with alkanols and alkylamines, especially alkanols and alkylamines having C₆-C₄₀-alkyl radicals, it is possible to obtain hydrophobicized products.

[0062] Hydrophilicized but nonionic products are obtainable by reaction of NCO-terminated polymers with polyether alcohols, for example di-, tri- or tetra- or polyethylene glycol.

[0063] Acid groups are incorporable for example by reaction with hydroxy carboxylic acids, hydroxysulfonic acids or amino acids. Examples of suitable reaction partners are 2-hydroxyacetic acid, 4-hydroxybenzoic acid, 12-hydroxy- dodecanoic acid, 2-hydroxyethanesulfonic acid, glycine or alanine.

[0064] Reaction with acrylate compounds such as alcohols containing acrylate groups, such as 2-hydroxyethyl acrylate or 2-hydroxyethyl methacrylate, makes it possible to obtain highly branched polyurethanes having polymerizable olefinic groups.

[0065] Oxidatively drying highly branched polyurethanes are obtainable by reacting initially mono- or polyunsaturated fatty acids, especially C₁₈-C₄₀ fatty acids, with an aliphatic alcohol having at least two OH groups, although at least one OH group must not be esterified. Linoleic acid, linolenic acid or oleic acid can be reacted by way of example. The fatty acid ester obtained, which still contains OH groups, is then reacted with NCO groups.

[0066] It is also possible to generate highly branched polyurethanes having different functionalities. This can be accomplished for example by reaction with a mixture of various compounds or else by reacting only a portion of the functional groups already present, for example only a portion of the OH and/or NCO groups.

[0067] Furthermore, one or more functional groups of the highly branched molecule can be reacted with reagents having affinity for the fiber, for example polymaines such as polyethyleneimine or polyvinylamine. A highly branched molecule containing a portion with affinity for the fiber as an anchoring group for the fiber is thereby obtained.

[0068] The transfunctionnalization of highly branched polyurethane may advantageously be effected immediately following the polymerization reaction without the NCO-terminated polyurethane being isolated beforehand. But the transfunctionnalization may also take place in a separate reaction.

[0069] The highly branched polyurethanes used according to the invention generally have on average at least 4 and not more than 200 functional groups. Highly branched polyurethanes preferably have from 4 to 150, particularly preferably from 4 to 100, functional groups. Preferred highly branched polyurethanes have a weight average molecular weight Mw of from 1 000 to 200 000 g/mol, preferably of from 1 000 to 100 000 g/mol.

[0070] This invention also provides for the use of highly branched polymers, especially highly branched polyurethanes, in finishes for wrinkleproofing cellulosic textiles. Finishes are any liquid formulations which contain the highly branched polymer, especially the highly branched polyurethane, 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 liquid textile treatment. Useful solvents include for example water, alcohols such as methanol, ethanol and propanol, THF or mixtures thereof. It is 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 highly branched polymers for example before or after home laundering, for example during ironing. But it is also possible to treat the textiles with highly branched polymers in the main wash cycle or after the main wash cycle in the refresher or rinse cycle of the washing machine.

[0071] 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.

[0072] The treatment before or after laundering may utilize a textile treatment which, as well as a highly branched polymer in dissolved or dispersed form, contains a surfactant. In this treatment, the cellulosic textiles are for example sprayed with the highly branched 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 a highly branched 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.

[0073] 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 highly branched polymers in dissolved or dispersed form according to the above-described process exhibit an excellent level of wrinkles and crease resistance that is durable to multiple laundering. There is frequently no longer any need to iron the textiles. The textiles thus treated additionally possess fiber and color protection.

[0074] The invention also provides a textile treatment comprising

[0075] a) from 0.1 to 40% by weight, preferably from 0.5 to 25% by weight, of at least one highly branched polymer, in particular at least one highly branched polyurethane,

[0076] b) from 0 to 30% by weight of one or more silicones,

[0077] c) from 0 to 30% by weight of one or more cationic and/or nonionic surfactants,

[0078] 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,

[0079] e) from 0 to 99.9% by weight of water,

[0080] components a) to e) adding up to 100% by weight.

[0081] Preferred silicones are amino-containing silicones, which are preferably present in microemulsified form, alkoxylated, especially ethoxylated, silicones, polyalkylene oxide-polysiloxanes, polyalkylene oxide-aminopolyalkylmethyl-ysiloxanes, 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'-dialkylaminoalkyl (meth)acrylates, N,N'-dialkylaminoalkyl(meth)acrylamides, (meth)acrylic acid, alkyl (meth)acrylates and/or vinylsulfonate. The aforementioned basic monomers may also be used in quaternized form.

[0082] A pretreatment formulation to be applied to the textile material by spraying may additionally include a spraying assistant. In some cases, it can 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.

[0083] 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.

[0084] The highly branched polymers may also be used when the textiles are washed in the main wash cycle of the washing machine.

[0085] The invention further provides a solid laundry detergent formulation comprising

[0086] a) from 0.05 to 20% by weight of at least one highly branched polymer, especially at least one highly branched polyurethane,

[0087] b) from 0 to 20% by weight of one or more silicones,

[0088] c) from 0.1 to 40% by weight of at least one nonionic and/or anionic surfactant,

[0089] d) from 0 to 50% by weight of one or more inorganic builders,

[0090] e) from 0 to 10% by weight of one or more organic builders,

[0091] f) from 0 to 60% by weight of other customary ingredients such as standardizers, enzymes, perfume, complexing agents, corrosion inhibitors, bleaches, bleach activators, bleach catalysts, cationic surfactants, dye transfer inhibitors, antiredeposition agents, soil release polymers, dyes, bactericides, dissolution improvers and/or disintegrants.

[0092] components a) to f) adding up to 100% by weight.

[0093] Useful anionic surfactants are in particular:

[0094] (fatty) alcohol sulfates of (fatty) alcohols having from 8 to 22, preferably from 10 to 18, carbon atoms, for example C<sub>8</sub>-C<sub>12</sub> alcohol sulfates, C<sub>12</sub>-C<sub>15</sub> alcohol sulfates, C<sub>15</sub>-C<sub>18</sub> alcohol sulfates, C<sub>18</sub>-C<sub>21</sub> alcohol sulfates, C<sub>21</sub>-C<sub>22</sub> alcohol sulfates, lauryl sulfate, cetyl sulfate, myristyl sulfate, palmityl sulfate, stearyl sulfate and tallow fatty alcohol sulfate;

[0095] sulfated alkoxylated C<sub>8</sub>-C<sub>22</sub> alcohols (alkyl ether sulfates). Compounds of this kind are prepared for example by first alkoxylating a C<sub>8</sub>-C<sub>22</sub> alcohol, preferably a C<sub>10</sub>-C<sub>18</sub> alcohol, for example a fatty alcohol, and then sulfating the alkoxylated product. The alkoxylated is preferably carried out using ethylene oxide;
[0096] linear C<sub>8</sub>- to C<sub>20</sub>-alkylbenzenesulfonates (LAS), preferably linear C<sub>8</sub>- to C<sub>13</sub>-alkylbenzenesulfonates and alkylolamidealkylbenzenesulfonates,

[0097] alkanesulfonates such as C<sub>8</sub>- to C<sub>24</sub>-alkanesulfonates, preferably C<sub>10</sub>- to C<sub>18</sub>-alkanesulfonates,

[0098] soaps such as, for example, the sodium and potassium salts of C<sub>8</sub>- to C<sub>2</sub>-carboxylic acids.

[0099] The anionic surfactants mentioned are preferably included in the laundry detergent in the form of salts. Suitable cations in these salts are alkali metal ions such as sodium, potassium and lithium and ammonium ions such as hydroxyethylammonium, di(hydroxyethyl)ammonium and tri(hydroxyethyl)ammonium.

[0100] Useful nonionic surfactants are in particular:

[0101] alkoxylated C<sub>8</sub>- to C<sub>24</sub>-alcohols such as fatty alcohol alkoxylates or oxo alcohol alkoxylates. These may have been alkoxylated with ethylene oxide, propylene oxide and/or butylene oxide. Useful surfactants here include all alkoxylated alcohols which contain at least two molecules of one of the aforementioned alkylene oxides. Here it is possible to use block polymers of ethylene oxide, propylene oxide and/or butylene oxide or addition products which contain the aforementioned alkylene oxides in random distribution. Nonionic surfactants generally contain from 2 to 50, preferably from 3 to 20, mol of at least one alkylene oxide per mole of alcohol. The alkylene oxide component is preferably ethylene oxide. The alcohols preferably have from 10 to 18 carbon atoms. Depending on the type of alkylolation catalyst used to make them, alkoxylates have a broad or narrow alkylene oxide homolog distribution;

[0102] alkylphenol alkoxylates such as alkylphenol ethoxylates having C<sub>8</sub>- to C<sub>4</sub>-alkyl chains and from 5 to 30 alkylene oxide units;

[0103] alkylpolyglycosides having from 8 to 22, preferably from 10 to 18, carbon atoms in the alkyl chain and generally from 1 to 20, preferably from 1.1 to 5, glycoside units;

[0104] N-alkylglycaminides, fatty acid amide alkoxylates, fatty acid alkanolamide alkoxylates and also block copolymers of ethylene oxide, propylene oxide and/or butylene oxide.

[0105] Useful inorganic builders are in particular:

[0106] crystalline or amorphous aluminosilicates having ion-exchanging properties such as zeolites in particular. Useful zeolites include in particular zeolites A, X, Y, 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;

[0107] crystalline silicates such as in particular disilicates or sheet-silicates, for example β-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> or β-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>. Silicates can be used in the form of their alkali metal, alkaline earth metal or ammonium salts, preferably as sodium, lithium or magnesium silicates;

[0108] amorphous silicates such as for example sodium metasilicate or ammonium disilicate;

[0109] 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;

[0110] polyphosphates such as for example pentasodium triphosphate.

[0111] Useful organic cobuilders include in particular low molecular weight, oligomeric or polymeric carboxylic acids.

[0112] Useful low molecular weight carboxylic acids include for example citric acid, hydrolytic modified citric acid such as for example agaric acid, malic acid, tartaric acid, gluconic acid, glutaric acid, succinic acid, imidodisuccinic acid, oxydisuccinic acid, propanetricarboxylic acid, butanetricarboxylic acid, cyclopentanetricarboxylic acid, alkyl- and alkenylsuccinic acids and aminopolycarboxylic acids such as for example nitrioltriacetic acid, β-alaninediacetic acid, ethylenediaminetetraacetic acid, serinediacetic acid, isoserenediacetic acid, N-(2-hydroxyethyl)iminodiacetic acid, ethylenediaminedisuccinic acid and methyl- and ethylenediaminediacetic acid;

[0113] useful oligomeric or polymeric carboxylic acids include for example homopolymers of acrylic acid, oligomaleic acids, copolymers of maleic acid with acrylic acid, methacrylic acid, C<sub>2</sub>-C<sub>20</sub>-olefins such as for example isobutene or long-chain α-olefins, vinyl alkyl ethers having C<sub>1</sub>-C<sub>8</sub>-alkyl groups, vinyl acetate, vinyl propionate, (meth)acrylic esters of C<sub>1</sub>- to C<sub>8</sub>-alcohols and styrene. Preference is given to using the homopolymers of acrylic acid and copolymers of acrylic acid with maleic acid. Polysarcinic acids are also useful as organic cobuilders. Oligomeric and polymeric carboxylic acids are used in acid form or as sodium salt.

[0114] Useful bleaches include for example adducts of hydrogen peroxide to inorganic salts such as sodium perborate monohydrate, sodium perborate tetrahydrate and sodium carbonate perhydrate and percarboxylic acids such as phthalimidopercarprionic acid.

[0115] Useful bleach activators include for example N,N,N’,N’-tetraacetylethylene diamine (TAEAD), sodium p-nonanoyloxybenzenesulfonate and N-methylmorpholinium acetonyltrimethylsulfate.

[0116] Preferable enzymes used in laundry detergents are proteases, lipases, amylases, cellulases, oxidases and peroxidases.

[0117] Useful dye transfer inhibitors include for example homopolymers and copolymers of 1-vinylpyrrolidone, of 1-vinylimidazole or of 4-vinylpyridine-N-oxide and homopolymers or copolymers of 4-vinylpyridine reacted with chloroacetic acid.

[0118] A solid laundry detergent formulation according to the invention is customarily present in powder or granule form or in extrudate or tablet form.
The invention further provides a liquid laundry detergent comprising

- from 0.05 to 20% by weight of at least one highly branched polymer, especially at least one highly branched polyurethane,
- from 0 to 20% by weight of one or more silicones,
- from 0.1 to 40% by weight of at least one nonionic and/or anionic surfactant,
- from 0 to 20% by weight of one or more inorganic builders,
- from 0 to 10% by weight of one or more organic cobuilders,
- from 0 to 60% by weight of other customary ingredients such as sodium carbonate, enzymes, perfume, complexing agents, corrosion inhibitors, bleach activators, bleach catalysts, cationic surfactants, dye transfer inhibitors, antiredeposition agents, soil release polymers, dyes, bactericides, unaqueous solvents, solubilizers, hydroxotropes, thickeners and/or alkanolamines,
- from 0 to 99.85% by weight of water,
- components a) to g) adding up to 100% by weight.

The above-mentioned silicones, nonionic and anionic surfactants, builders and cobuilders may be used.


The concentration of the highly branched polymers in the wash liquor is for example in the range from 10 to 5000 ppm, preferably in the range from 50 to 1000 ppm. Textiles treated with the highly branched polymers in the main wash cycle of the 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 their fiber and color protection, look less used, i.e. exhibit less fluff and fewer knots and less color damage or fading, after repeated washing.

The highly branched polymers may be used in the rinse or refresher cycle following the main wash cycle. The concentration of the highly branched polymers in the wash liquor is for example in the range from 10 to 5000 ppm, preferably in the range from 50 to 1000 ppm. The rinse liquor may if desired include ingredients typical for a fabric conditioner or refresher. Textiles treated in this way and then dried on the line or preferably in a tumble dryer likewise exhibit a very high level of crease resistance that is associated with the positive effects on ironing that were described above. 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.

The invention also provides a laundry refresher comprising

- from 0.05 to 40% by weight of at least one highly branched polymer, especially of at least one highly branched polyurethane,
- from 0 to 20% by weight of one or more silicones,
- from 0.1 to 40% by weight of at least one cationic surfactant,
- from 0 to 30% by weight of one or more nonionic surfactants and
- from 0 to 30% by weight of other customary ingredients such as silicones, other lubricants, wetting agents, film-forming polymers, scents, dyes, stabilizers, fiber and color protection additives, viscosity modifiers, soil release additives, corrosion control additives, bactericides and preservatives, and
- from 0 to 99.85% by weight of water,
- components a) to f) adding up to 100% by weight.

Preferred cationic surfactants are selected from the group of the quaternary diester ammonium salts, the quaternary tetraalkylammonium salts, the quaternary diamidoammonium 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 quaternary diester ammonium salts which have two C1-C2-alk(en)ylcarboxamidoxy(mono- or dihydroxyalkyl) radicals and two C1-C2-alkyl or -hydroxyalkyl radicals on the quaternary nitrogen atom and, for example, chloride, bromide, methosulfate or sulfate as counterion.

Quaternary diester ammonium salts further include in particular those which have a C1-C2-alk(en)ylcarboxyloxymethylene radical bearing a C1-C2-alk(en)ylcarboxyloxy radical on the central carbon atom of the trimethylene group and three C1-C2-alk(en)yl or -hydroxyalkyl radicals on the quaternary nitrogen atom and, for example, chloride, bromide, methosulfate or sulfate as counterion.

Quaternary tetraalkylammonium salts are in particular those which have two C1-C2-alk(en)yl radicals and two C1-C2-alk(en)yl radicals on the quaternary nitrogen atom and, for example, chloride, bromide, methosulfate or sulfate as counterion.

Quaternary diamidoammonium salts are in particular those which bear two C1-C2-alk(en)ylcarboxyamino(mono- or trimethylene) radical, a C1-C2-alk(en)ylcarboxyloxy(mono- or trimethylene) radical and a methyl group as substituents on the nitrogen atom.

Amidoamine esters are in particular tertiary amines bearing a C1-C2-alk(en)ylcarboxyamino(mono- or trimethylene) radical, a C1-C2-alk(en)ylcarboxyloxy(mono-or trimethylene) radical and a methyl group as substituents on the nitrogen atom.

Imidazolinium salts are in particular those which bear a C1-C2-alk(en)yl radical in position 2 of the heterocycle, a C1-C2-alk(en)ylcarboxyloxy or amino-
ethylene 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.

[0146] The examples hereinbelow illustrate the invention.

EXAMPLES

[0147] The percentages in the examples are by weight, unless the context suggests otherwise.

[0148] The following finishes were used:

Finish A

[0149] 1% by weight alkaline solution of the highly branched polyurethane A, which was prepared as follows:

[0150] 168 g of hexamethylene diisocyanate (HDI), dissolved in 386 g of dimethylacetamide (DMAc), were initially charged at room temperature under nitrogen. 134 g of dimethylpropionic acid dissolved in 313 g of DMAc were then added in the course of 1 min with intensive stirring. After metered addition of 0.2 g of dibutyltin dilaurate, the reaction mixture was heated to 70°C and the decrease in the NCO content was followed titrimetrically. When an NCO content of 1.5% by weight had been reached, the reaction product had an average functionality of 1 with regard to NCO, of 3 with regard to COOH and of 1 with regard to OH.

[0151] This polyaddition product was then admixed with 22 g of trimethylolpropane (TMP) dissolved in 50 g of DMAc and subsequently stirred at 70°C for 3 h. During this period, the NCO content of the mixture decreased to 0%. The product was then stripped of solvent in a rotary evaporator at 80°C under reduced pressure.

[0152] The solid end product had the following parameters:

[0153] Average functionality with regard to OH: about 5 and with regard to COOH: about 9 Average molar mass: 6 018 g/mol

Finish B

[0154] 1% by weight alkaline solution of the highly branched polyurethane B, which was prepared as follows:

[0155] 336 g of hexamethylene diisocyanate (HDI), dissolved in 336 g of dimethylacetamide (DMAc), were initially charged at 0°C under nitrogen. 105 g of diethanolamine were then added in the course of 20 min with intensive stirring and stirred at 0°C for a further 30 min. Then 134 g of dimethylpropionic acid, dissolved in 239 g of DMAc, were added. After metered addition of 0.5 g of dibutyltin dilaurate, the reaction mixture was heated to 60°C and the decrease in the NCO content was followed titrimetrically. When an NCO content of 1.2% by weight had been reached, an excess of methanol was added to convert NCO groups still present. The product was then stripped of solvent in a rotary evaporator at 80°C under reduced pressure.

[0156] The reaction product had the following parameters:

[0157] Average functionality with regard to COOH: about 3 and with regard to OH: about 4 Average molar mass: 1 757 g/mol

Finish C

[0158] 1% by weight alkaline solution of the highly branched polyurethane C, which was prepared as follows:

[0159] 222 g of isophorone diisocyanate (IPDI) were initially charged under nitrogen. A mixture of 67 g of TMP and 67 g of dimethylpropionic acid, dissolved in 365 g of DMAc, was then added in the course of 1 min with intensive stirring. After metered addition of 0.4 g of dibutyltin dilaurate, the reaction mixture was heated to 60°C, stirred at this temperature and the decrease in the NCO content was followed titrimetrically. When an NCO content of 1.0% by weight had been reached, the reaction product had an average functionality of 1 with regard to NCO, of 3 with regard to COOH and of 4 with regard to OH.

[0160] This polyaddition product was then admixed with 32 g of polytetrahydrofuran with an average molar mass of 250 g/mol and subsequently stirred at 60°C for 3 h. During this period, the NCO content of the mixture decreased to 0%. The product was then stripped of solvent in a rotary evaporator at 80°C under reduced pressure.

[0161] The solid end product had the following parameters:

[0162] Average functionality with regard to OH: about 20 and with regard to COOH: about 15 Average molecular weight: 22 610 g/mol

Finish D

[0163] 1% by weight alkaline solution of the highly branched polyurethane D, which was prepared as follows:

[0164] 168 g of hexamethylene diisocyanate (HDI), dissolved in 168 g of dimethylacetamide (DMAc), were initially charged at 0°C under nitrogen. 52.5 g of diethanolamine dissolved in 52.5 g of DMAc were then added at 0°C in the course of 20 min with intensive stirring and stirred at 0°C for a further 30 min. Then 59.9 g of N-methyl-diethanolamine, dissolved in 59.5 g of DMAc, were added. After metered addition of 0.2 g of dibutyltin dilaurate, the reaction mixture was heated to 40°C and the decrease in the NCO content was followed titrimetrically. When an NCO content of 1.2% by weight had been reached, an excess of methanol was added to convert NCO groups still present. The product was then stripped of solvent in a rotary evaporator at 80°C under reduced pressure.

[0165] The reaction product had the following parameters:

[0166] Average functionality with regard to NR, about 3 and with regard to OH: about 4 Average molar mass: 1 782 g/mol

Finishing of Fabric Samples

[0167] Cotton fabrics having the size reported in table 1 and a basis weight of 160 g/m² were sprayed on both sides
with the finishes A, B, C and D in such a way that the add-on was 2%, based on the particular weight of the dry textile material, and then hot pressed while still slightly moist.

[0168] 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 washing 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 sheet-like 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 the rating of 5 was awarded to wrinkle- and crease-free fabric. The fabric samples pretreated with the finishes A, B and C received ratings between 2.5 and 3.5. In contrast, the untreated fabric samples each received a rating of 1.

| TABLE 1 |
|---------------------------------|-----------------|-----------------|-----------------|
| | Cotton (40 cm x 40 cm) | Cotton (40 cm x 40 cm) | Cotton (40 cm x 80 cm) |
| Untreated | 3 | 1 | 1 |
| A | 3.5 | 3 | 3 |
| B | 3 | 2.5 | 3 |
| C | 2.5 | 2.5 | 2.5 |
| D | 3 | 2.5 | 3 |

We claim:
1. A process for wrinkleproofing cellulosic textiles by treating the textiles with a finish and drying the treated textiles, which comprises using a finish comprising one or more highly branched polymers in dissolved or dispersed form.
2. A process as claimed in claim 1, wherein the highly branched polymers are highly branched polyurethanes.
3. A process as claimed in either of claims 1 and 2, wherein the highly branched polymers contain one or more functional groups selected from the group consisting of —COOH, —COOR, —CONHR, —CONH₂, —OH, —SH, —NH₂, —NH₃, —NR₂, —NR₃⁺, —SO₃H, —SO₃R, —NCOOR, —NCONH₂, —NCONHR and salts thereof.
4. A process as claimed in claim 3, wherein the functional groups are selected from the group consisting of —COOH, CONH₂, —OH, —NH₂, —NH₃, —NR₂, —NR₃⁺, —SO₃H and salts thereof.
5. A process as claimed in claim 4, wherein the functional groups are selected from the group consisting of —COOH, —OH, —SO₃H and salts thereof.
6. A process as claimed in claim 4, wherein the functional groups are selected from the group consisting of —NH₂, —NH₃, —NR₂, —NR₃⁺ and salts thereof.
7. A process as claimed in any of claims 1 to 6, wherein the highly branched polymers contain on average at least 4 functional groups.
8. A process as claimed in claim 7, wherein the highly branched polymers contain on average from 4 to 100 functional groups.
9. The use of highly branched polymers as defined in any of claims 1 to 8 in textile treatments, solid and liquid laundry detergents and laundry refreshers.
10. The use of finishes comprising highly branched polymers as defined in any of claims 1 to 8 in the manufacture of textiles, textile treatment, main laundry cycle, final laundry rinse cycle and ironing.
11. A finish for wrinkleproofing cellulosic textiles, comprising highly branched polymers as defined in any of claims 1 to 8.
12. A textile treatment comprising
   a) from 0.1-40% by weight of at least one highly branched polymer as defined in any of claims 1 to 8,
   b) from 0 to 30% by weight of one or more silicones,
   c) from 0 to 30% by weight of one or more 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 ing assistants, and
   c) from 0 to 99.9% by weight of water,
   components a) to e) adding up to 100% by weight.
13. A solid laundry detergent comprising
   a) from 0.05 to 20% by weight of at least one highly branched polymer as defined in any of claims 1 to 8,
   b) from 0 to 20% by weight of one or more silicones,
   c) from 0.1 to 40% by weight of at least one nonionic and/or anionic surfactant,
   d) from 0 to 50% by weight of one or more inorganic builders,
   e) from 0 to 10% by weight of one or more organic copolymers,
   f) from 0 to 60% by weight of other customary ingredients such as standardizers, enzymes, perfume, complexing agents, corrosion inhibitors, bleaches, bleach activators, cationic surfactants, bleach catalysts, dye transfer inhibitors, antideposition agents, soil release polymers, dyes, bactericides, dissolution improvers and/or disintegrants, components a) to f) adding up to 100% by weight.
14. A liquid laundry detergent comprising
   a) from 0.05 to 20% by weight of at least one highly branched polymer as defined in any of claims 1 to 8,
   b) from 0 to 20% by weight of one or more silicones,
   c) from 0.1 to 40% by weight of at least one nonionic and/or anionic surfactant,
   d) from 0 to 20% by weight of one or more inorganic builders,
   e) from 0 to 10% by weight of one or more organic copolymers,
   f) from 0 to 60% by weight of other customary ingredients such as sodium carbonate, enzymes, perfume, complexing agents, corrosion inhibitors, bleaches, bleach activators, bleach catalysts, cationic surfactants, dye transfer inhibitors, antideposition agents, soil release...
polyesters, dyes, bactericides, aqueous solvents, solubilizers, hydrodopes, thickeners and/or alkanealines,
g) from 0 to 99.85% by weight of water,
components a) to g) adding up to 100% by weight.
15. A laundry refresher comprising
a) from 0.05 to 40% by weight of at least one highly branched polymer, especially of at least one highly branched polyurethane,
b) from 0 to 20% by weight of one or more silicones,
c) from 0.1 to 40% by weight of at least one cationic surfactant,
d) from 0 to 30% by weight of one or more nonionic surfactants,
c) from 0 to 30% by weight of other customary ingredients such as silicones, other lubricants, wetting agents, film-forming polymers, scents, dyes, stabilizers, fiber and color protection additives, viscosity modifiers, soil release additives, corrosion control additives, bactericides and preservatives, and
f) from 0 to 99.85% by weight of water,
components a) to f) adding up to 100% by weight.
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