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(54) **HYDROPHILICALLY MODIFIED
POLYISOCYANATES AND
POLYURETHANES FOR
CREASE-PROOFING TEXTILES
CONTAINING CELLULOSE**

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(57) **ABSTRACT**

A process for wrinkleproofing cellulosic textiles by treating the textiles with a finish and drying the treated textiles, whereby said finish comprises (A) one or more hydrophilic modified polyisocyanates and/or (B) one or more polyurethanes in dissolved or dispersed form.

**HYDROPHILICALLY MODIFIED
POLYISOCYANATES AND POLYURETHANES FOR
CREASE-PROOFING TEXTILES CONTAINING
CELLULOSE**

[0001] This invention relates to processes for wrinkleproofing cellulosic textiles, wrinkleproofing finishes comprising hydrophilic modified polyisocyanates and/or polyurethanes, the use of the finishes and of the polyisocyanates and polyurethanes, and also textile treatments, solid and liquid laundry detergents and laundry refreshers comprising same.

[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 a 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, shape retention polymers, 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.

[0007] EP-A 0 978 556 describes a mixture of a softener and a crosslinker component having cationic properties as a fabric wrinkle and crease control composition and also a method of wrinkleproofing textiles.

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

[0009] We have found that this object is achieved by a process for wrinkleproofing cellulosic textiles by treating the textiles with a finish and drying the treated textiles, which said finish comprises (A) one or more hydrophilic modified polyisocyanates and/or (B) one or more polyurethanes in dissolved or dispersed form.

[0010] The invention also provides a wrinkleproofing finish for cellulosic textiles that comprises hydrophilic modified polyisocyanates and polyurethanes.

[0011] Hydrophilic Modified Polyisocyanates

[0012] The finish of the invention may include (A) one or more hydrophilic modified polyisocyanates.

[0013] The hydrophilic modified polyisocyanates to be used according to this invention are based on customary

diisocyanates and/or customary higher functional polyisocyanates having an average NCO functionality of from 2.0 to 4.5. These components can be present alone or mixed.

[0014] Examples of customary diisocyanates are aliphatic diisocyanates such as tetramethylene diisocyanate, hexamethylene diisocyanate (1,6-diisocyanatohexane), octamethylene diisocyanate, decamethylene diisocyanate, dodecamethylene diisocyanate, tetradecamethylene diisocyanate, trimethylhexane diisocyanate or tetramethylhexane diisocyanate, cycloaliphatic diisocyanates such as 1,4-, 1,3- or 1,2-diisocyanatocyclohexane, 4,4'-di(isocyanatocyclohexyl)methane, 1-isocyanato-3,3,5-trimethyl-5-(isocyanatomethyl)cyclohexane (isophorone diisocyanate) or 2,4- or 2,6-diisocyanato-1-methylcyclohexane and also aromatic diisocyanates such as 2,4- or 2,6-tolylene diisocyanate, tetramethylxylene diisocyanate, p-xylene diisocyanate, 2,4'- or 4,4'-diisocyanatodiphenylmethane, 1,3- or 1,4-phenylene diisocyanate, 1-chloro-2,4-phenylene diisocyanate, 1,5-naphthylene diisocyanate, diphenylene 4,4'-diisocyanate, 4,4'-diisocyanato-3,3'-dimethyldiphenyl, 3-methyldiphenylmethane 4,4'-diisocyanate or diphenyl ether 4,4'-diisocyanate. It is also possible for mixtures of the diisocyanates mentioned to be present. Preference is given among these to aliphatic diisocyanates, in particular to hexamethylene diisocyanate and isophorone diisocyanate.

[0015] Suitable customary higher functional polyisocyanates are for example triisocyanates such as 2,4,6-triisocyanatotoluene or 2,4,4'-triisocyanatodiphenyl ether or the mixtures of di-, tri- and higher polyisocyanates which are obtained by phosgenation of corresponding aniline/formaldehyde condensates and are methylene-bridged polyphenyl polyisocyanates.

[0016] Of particular interest are customary aliphatic higher functional polyisocyanates of the following groups:

[0017] (a) isocyanurate-group-containing polyisocyanates of aliphatic and/or cycloaliphatic diisocyanates. Particular preference amongst these is given to the corresponding isocyanato-isocyanurates based on hexamethylene diisocyanate and isophorone diisocyanate. The present isocyanurates are in particular simple trisisocyanatoalkyl or triisocyanatocycloalkyl isocyanurates which are cyclic trimers of the diisocyanates, or mixtures with their higher homologs having more than one isocyanurate ring. The isocyanato-isocyanurates generally have an NCO content of from 10 to 30% by weight, in particular of from 15 to 25% by weight, and an average NCO functionality of from 2.6 to 4.5.

[0018] (b) Uretidione-group-containing polyisocyanates having aliphatically and/or cycloaliphatically bound isocyanate groups, preferably derived from hexamethylene diisocyanate or isophorone diisocyanate. Uretidiones are cyclic dimerization products of two NCO groups.

[0019] (c) Biuret-group-containing polyisocyanates having aliphatically bound isocyanate groups, in particular tris(6-isocyanatoethyl) biuret or its mixtures with its higher homologs. These biuret-group-containing polyisocyanates generally have an NCO content of from 18 to 25% by weight and an average NCO functionality of from 3 to 4.5.

[0020] (d) Urethane- and/or allophanate-group-containing polyisocyanates with aliphatically or cycloaliphatically bound isocyanate groups, as obtainable for example by reacting excess amounts of hexamethylene diisocyanate or

isophorone diisocyanate with simple polyhydric alcohols such as trimethylolpropane, glycerol, 1,2-dihydroxypropane or mixtures thereof. These urethano- and/or allophanato-containing polyisocyanates generally have an NCO content of from 12 to 20% by weight and an average NCO functionality of from 2.5 to 3.

[0021] (e) Oxadiazinetrione-group-containing polyisocyanates, preferably derived from hexamethylene diisocyanate or isophorone diisocyanate. Such oxadiazinetrione-containing polyisocyanates are preparable from diisocyanate and carbon dioxide.

[0022] (f) Urethaneimine-modified polyisocyanates.

[0023] For the use according to the present invention, the described diisocyanates and/or higher functionalized polyisocyanates are converted into nonionically hydrophilic modified polyisocyanates, which are particularly preferred for the use according to the present invention, by reaction with NCO-reactive compounds containing hydrophilicizing structural elements with nonionic groups or with polar groups which cannot be converted into ionic groups. In this reaction, the diisocyanate or polyisocyanate, as the case may be, is present in stoichiometric excess in order that the resulting hydrophilic modified polyisocyanate may still contain free NCO groups.

[0024] Suitable for use as such NCO-reactive compounds with hydrophilicizing structural elements are in particular hydroxyl-terminated polyethers of the general formula I



[0025] where

[0026] R^8 is C_1 - C_{20} -alkyl, in particular C_1 - C_4 -alkyl, or C_2 - C_{20} -alkenyl, cyclopentyl, cyclohexyl, glycidyl, oxetyl, phenyl, tolyl, benzyl, furfuryl or tetrahydrofurfuryl,

[0027] E is sulfur or in particular oxygen,

[0028] D is propylene or especially ethylene, including in particular block-mixed ethoxylated and propoxylated compounds, and

[0029] n is from 5 to 120, in particular 10 to 25.

[0030] The use of nonionically hydrophilic modified polyisocyanates which contain the polyethers I therefore also constitutes a preferred embodiment.

[0031] These are particularly preferably C_1 - C_4 -alkanol-based ethylene oxide or propylene oxide polyethers having average molecular weights from 250 to 7 000, in particular from 450 to 1 500.

[0032] It is also possible to first react the described diisocyanates and/or higher functionalized polyisocyanates with a deficiency of hydroxyl-terminated polyesters, of other hydroxyl-terminated polyethers, or of polyols, for example ethylene glycol, trimethylolpropane or butanediol, to form prepolymers and then react these prepolymers subsequently or else simultaneously with the polyethers I in deficiency to form the hydrophilic modified polyisocyanates having free NCO groups.

[0033] It is also possible to prepare nonionically hydrophilic modified polyisocyanates from diisocyanate or polyisocyanate and polyalkylene glycols of the formula HO-

$(DO)_n-H$, where D and n are each as defined above. In this reaction, the two terminal OH groups of the polyalkylene glycol both react with isocyanate.

[0034] The recited types of nonionically hydrophilic modified polyisocyanates are more particularly described in DE-A 24 47 135, DE-A 26 10 552, DE-A 29 08 844, EP-A 0 13 112, EP-A 019 844, DE-A 40 36 927, DE-A 41 36 618, EP-B 206 059, EP-A 464 781 and EP-A 516 361.

[0035] The described diisocyanates and/or higher functionalized polyisocyanates are converted into anionically hydrophilic modified polyisocyanates by reaction with NCO-reactive compounds containing hydrophilicizing anionic groups, in particular acid groups such as carboxyl groups, sulfonic acid groups or phosphonic acid groups. In this reaction, the diisocyanate or polyisocyanate is present in stoichiometric excess in order that the resulting hydrophilic modified polyisocyanate may still contain free NCO groups.

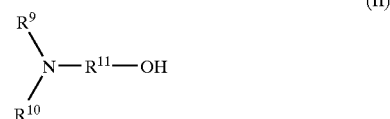
[0036] Suitable NCO-reactive compounds with anionic groups include in particular hydroxycarboxylic acids such as 2-hydroxyacetic acid, 3-hydroxypropionic acid, 4-hydroxybutyric acid or hydroxypivalic acid and 2,2,2-tris- and also 2,2-bis(hydroxymethyl)alkanoic acids, for example 2,2-bis(hydroxymethyl)acetic acid, 2,2-bis(hydroxymethyl)propionic acid, 2,2-bis(hydroxymethyl)butyric acid or 2,2,2-tris(hydroxymethyl)acetic acid. The carboxyl groups can be partly or wholly base-neutralized to be present in a water-soluble or water-dispersible form. The base used here is preferably a tertiary amine, which is known to be inert toward isocyanate.

[0037] The described diisocyanates and/or higher functionalized polyisocyanates can also be reacted with a mixture of nonionically hydrophilic-modifying and anionically hydrophilic-modifying compounds, which are added in succession or simultaneously, for example with a deficiency of the polyethers I and the described hydroxycarboxylic acids.

[0038] The recited types of anionically hydrophilic modified polyisocyanates are more particularly described in DE-A 40 01 783, DE-A 41 13 160 and DE-A 41 42 275.

[0039] The described diisocyanates and/or higher functionalized polyisocyanates are converted into cationically hydrophilic modified polyisocyanates by reaction with NCO-reactive compounds containing chemically built-in alkylatable or protonatable functions to form a cationic center. These functions are in particular tertiary nitrogen atoms, which are known to be inert toward isocyanate and to be readily quaternizable or protonatable. In the reaction of diisocyanate or polyisocyanate with these NCO-reactive compounds, the former are present in excess in order that the resulting hydrophilic modified polyisocyanate may still contain free NCO groups.

[0040] Suitable such NCO-reactive compounds with tertiary nitrogen atoms are preferably aminoalcohols of the general formula II



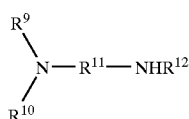
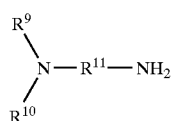
[0041] where

[0042] R^9 and R^{10} are each linear or branched C_1 - C_{20} -alkyl, in particular C_1 - C_5 -alkyl, or are together combined with the nitrogen atom into a five- or six-membered ring which may additionally contain an oxygen atom or a tertiary nitrogen atom, in particular a piperidine, morpholine, piperazine, pyrrolidine, oxazoline or dihydrooxazine ring, in which case the radicals R^9 and R^{10} may additionally carry hydroxyl groups, in particular one hydroxyl group each, and

[0043] R^{11} is C_2 - C_{10} -alkylene, in particular C_2 - C_6 -alkylene, which can be linear or branched.

[0044] Suitable aminoalcohols II are in particular N-methyldiethanolamine, N-methyldi(iso)propanolamine, N-butyldiethanolamine, N-butyldi(iso)propanolamine, N-stearyldiethanolamine, N-stearyldi(iso)propanolamine, N,N-dimethylethanolamine, N,N-dimethyl(iso)propanolamine, N,N-diethylethanolamine, N,N-diethyl(iso)propanolamine, N,N-dibutylethanolamine, N,N-dibutyl(iso)propanolamine, triethanolamine, tri(iso)propanolamine, N-(2-hydroxyethyl)morpholine, N-(2-hydroxypropyl)morpholine, N-(2-hydroxyethyl)piperidine, N-(2-hydroxypropyl)piperidine, N-methyl-N'-(2-hydroxyethyl)piperazine, N-methyl-N'-(2-hydroxypropyl)piperazine, N-methyl-N'-(4-hydroxybutyl)piperazine, 2-hydroxyethyloxazoline, 2-hydroxypropyloxazoline, 3-hydroxypropyloxazoline, 2-hydroxyethyldihydrooxazine, 2-hydroxypropyldihydrooxazine or 3-hydroxypropyldihydrooxazine.

[0045] Suitable such NCO-reactive compounds with tertiary nitrogen atoms further include preferably diamines of the general formula IIIa or IIIb



[0046] where R^9 to R^{11} are each as defined above and R^{12} is C_1 - C_5 -alkyl or is combined with R^9 into a five- or six-membered ring, in particular into a piperazine ring.

[0047] Suitable diamines IIIa are in particular N,N-dimethyl-ethylenediamine, N,N-diethylethylenediamine, N,N-dimethyl-1,3-diamino-2,2-dimethylpropane, N,N-diethyl-1,3-propylenediamine, N-(3-aminopropyl)morpholine, N-(2-aminopropyl)morpholine, N-(3-aminopropyl)piperidine, N-(2-aminopropyl)piperidine, 4-amino-(N,N-diethylamino)pentane, 2-amino-1-(N,N-dimethylamino)propane, 2-amino-1-(N,N-diethylamino)propane or 2-amino-1-(N,N-diethylamino)-2-methylpropane.

[0048] Suitable diamines IIIb include in particular N,N,N'-trimethylethylenediamine, N,N,N'-triethylethylenediamine, N-methylpiperazine or N-ethylpiperazine.

[0049] Further usable NCO-reactive compounds include polyether(poly)ols with built-in tertiary nitrogen atoms which are preparable by propoxylation and/or ethoxylation of initiator molecules containing amine nitrogen. Such polyether(poly)ols are for example the propoxylation and ethoxylation products of ammonia, ethanolamine, diethanolamine, ethylenediamine or N-methylaniline.

[0050] Other usable NCO-reactive compounds are polyester and polyamide resins with tertiary nitrogen atoms, urethano-containing polyols with tertiary nitrogen atoms, and also polyhydroxypolyacrylates with tertiary nitrogen atoms.

[0051] The described diisocyanates and/or higher functionalized polyisocyanates can also be reacted with a mixture of nonionically hydrophilic-modifying and cationically hydrophilic-modifying compounds, which are added in succession or simultaneously, for example with a deficiency of the polyethers I and the aminoalcohols II or the diamines IIIa or IIIb. It is also possible to use mixtures of nonionically hydrophilic-modifying and anionically hydrophilic-modifying compounds.

[0052] The recited types of cationically hydrophilic modified polyisocyanates are more particularly described in DE-A 42 03 510 and EP-A 531 820.

[0053] Since the hydrophilic modified polyisocyanates mentioned (A) can in general be used in aqueous media, adequate dispersibility of the polyisocyanates must be ensured. Preferably, within the group of the described hydrophilic modified polyisocyanates, certain reaction products of di- or polyisocyanates and hydroxyl-terminated polyethers (polyether alcohols) such as the compounds I act as emulsifiers for this purpose.

[0054] The good results which are obtained with the hydrophilic modified polyisocyanates (A) in aqueous media are all the more surprising since it had to be expected that isocyanates would rapidly decompose in aqueous medium. Yet, the polyisocyanates used according to this invention have a pot life of several hours in the aqueous liquor; that is, the instant polyisocyanate dispersions are stable during the customary processing time. A dispersion is said to be stable when its components remain dispersed in one another without their separating into discrete layers. By "pot life" is meant the time during which the dispersions remain processible before they gel and set. Aqueous isocyanate dispersions gel and set because a reaction takes place between the water and the isocyanate to form a polyurea.

[0055] Polyurethanes

[0056] The finish of the invention may comprise (B) one or more polyurethanes.

[0057] By polyurethanes are meant systems constructed from polyisocyanates (hereinafter also called monomers I) and polyisocyanate-reactive compounds having at least one hydroxyl group and optionally compounds having at least one primary or secondary amino group. Polyurethanes generally no longer contain any free isocyanate groups.

[0058] Useful polyisocyanates for preparing the polyurethanes (B) in the finish include customary diisocyanates and/or customary more highly functional polyisocyanates as described under the hydrophilic modified polyisocyanates

(A). Here too preference is given to aliphatic diisocyanates and aliphatic more highly functional polyisocyanates.

[0059] The further constructional components of the polyurethane include initially polyols having a molecular weight of from 400 to 6 000 g/mol, preferably from 600 to 4 000 g/mol (monomers II).

[0060] Polyetherpolyols or polyesterpolyols are contemplated in particular.

[0061] Polyesterdiols are in particular the well-known reaction products of dihydric alcohols with dibasic carboxylic acids. Instead of the free polycarboxylic acids it is also possible to use the corresponding polycarboxylic anhydrides or corresponding polycarboxylic esters of lower alcohols or mixtures thereof to prepare the polyesterpolyols. The polycarboxylic acids can be aliphatic, cycloaliphatic, aromatic or heterocyclic and can be unsaturated and/or substituted, for example by halogen atoms. Examples are succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, tetrachlorophthalic anhydride, endomethylenetetrahydrophthalic anhydride, glutaric anhydride, maleic acid, maleic anhydride, fumaric acid, dimeric fatty acids. Useful polyhydric alcohols include for example ethylene glycol, (1,2)-propylene glycol, (1,3)-propylene glycol, (1,4)-butanediol, (1,3)-butanediol, (1,4)-butenediol, (1,4)-butyndiol, (1,5)-pentanediol, (1,6)-hexanediol, (1,8)-octanediol, neopentylglycol, cyclohexanedimethanol, (1,4-bishydroxymethylcyclohexane), 2-methyl-1,3-propanediol, (1,5)-pentanediol, also diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, dipropylene glycol, polypropylene glycol, dibutylene glycol and polybutylene glycols.

[0062] It is also possible to use lactone-based polyesterdiols, i.e., homo- or interpolymers of lactones, preferably terminally hydroxyl-functional addition products of lactones or lactone mixtures, for example ϵ -caprolactone, β -propiolactone, γ -butyrolactone and/or methyl- ϵ -caprolactone, on suitable difunctional base molecules, for example the low molecular weight dihydric alcohols mentioned above as a constructional component for polyesterpolyols. The corresponding addition polymers of ϵ -caprolactone are particularly preferred. Similarly, lower polyesterdiols or polyetherdiols can be used as bases for preparing the lactone addition polymers. Instead of the addition polymers of lactones it is also possible to use the corresponding, chemically equivalent polycondensates of the hydroxycarboxylic acids corresponding to the lactones.

[0063] Useful polyetherdiols, alone or mixed with polyesterdiols, are obtainable in particular by homopolymerization of ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, styrene oxide or epichlorohydrin, for example in the presence of BF_3 , or by addition of these compounds, optionally mixed or in succession, to base components having reactive hydrogen atoms, such as alcohols or amines, e.g., water, ethylene glycol, (1,3)-propylene glycol, (1,2)-propylene glycol, 4,4'-dihydroxydiphenylpropane and aniline.

[0064] The fraction of the above-described monomers II is generally in the range from 0.1 to 0.8 gram equivalent, preferably from 0.2 to 0.7 gram equivalent, of the hydroxyl group of the monomer II based on 1 gram equivalent of isocyanate of the polyisocyanate.

[0065] Further constructional components of the polyurethane include chain extenders or crosslinkers having at least two isocyanate-reactive groups selected from hydroxyl groups and primary or secondary amino groups.

[0066] There may be mentioned polyols, especially diols and triols, having a molecular weight below 400 g/mol to 62 g/mol (monomers III).

[0067] Useful polyols include in particular the above-recited diols and triols suitable for preparing polyesterpolyols and also more than trifunctional alcohols such as pentaerythritol or sorbitol.

[0068] The fraction of monomer III is generally in the range from 0 to 0.8, especially from 0 to 0.7, gram equivalent, based on 1 gram equivalent of isocyanate.

[0069] The optional monomers IV are at least difunctional amine chain extenders or crosslinkers of the molecular weight range from 32 to 500 g/mol, preferably from 60 to 300 g/mol, which contain at least two primary, two secondary or one primary and one secondary amino group.

[0070] Examples thereof are diamines, such as diaminoethane, diaminopropanes, diaminobutanes, diaminohexanes, piperazine, 2,5-dimethylpiperazine, amino-3-aminomethyl-3,5,5-trimethylcyclohexane (isophoronediamine, IPDA), 4,4'-diaminodicyclohexylmethane, 1,4-diaminocyclohexanes, aminoethylethanolamine, hydrazine, hydrazine hydrate or triamines such as diethylenetriamine or 1,8-diamino-4-aminomethyloctane. Amino-containing chain extenders may also be used in blocked form, for example in the form of the corresponding ketimines (see for example CA-1 129 128), ketazines (cf. for example U.S. Pat. No. 4,269,748) or amine salts (see U.S. Pat. No. 4,292,226). Similarly, oxazolidines as used for example in U.S. Pat. No. 4,192,937, are capped polyamines which can be used to chain extend the prepolymers in the preparation of the polyurethanes of the present invention. When such capped polyamines are used, they are generally mixed with the prepolymers in the absence of water and this mixture is subsequently mixed with the dispersion water or a portion of the dispersion water, so that the corresponding polyamine intermediates are released hydrolytically.

[0071] Preference is given to using mixtures of di- and triamines, particularly preferably mixtures of isophoronediamine and diethylenetriamine.

[0072] The monomers V, optionally likewise used as chain extenders, are aminoalcohols having a hydroxyl group and a primary or secondary amino group such as ethanolamine, isopropanolamine, methylethanolamine or aminoethoxyethanol.

[0073] The fraction of monomer IV or V is in each case preferably in the range from 0 to 0.4, particularly preferably from 0 to 0.2, gram equivalent, based on 1 gram equivalent of isocyanate of the polyisocyanate.

[0074] Useful constructional components further include compounds which have at least one, preferably two, isocyanate-reactive groups, i.e., hydroxyl or primary or secondary amino groups, and additionally, in contrast to the above-described monomers, ionic groups or potentially ionic

groups which are convertible into ionic groups by a simple neutralizing or quaternizing reaction (monomers VI). The introduction of monomers VI renders the polyurethanes self-dispersible, i.e., no dispersing aids such as protective colloids or emulsifiers are needed for dispersion in water in this case.

[0075] Cationic or anionic groups may be introduced by using compounds having (potential) cationic or (potential) anionic groups and isocyanate-reactive hydrogen atoms. These groups of compounds include for example polyethers having tertiary nitrogen atoms and preferably two terminal hydroxyl groups, as are obtainable for example in a conventional manner by alkoxylation of amines having two hydrogen atoms attached to the amine nitrogen, for example methylamine, aniline or N,N'-dimethylhydrazine. Polyethers of this kind generally have a molecular weight within the range from 500 to 6 000 g/mol.

[0076] Preferably, however, the ionic groups are introduced by using comparatively low molecular weight compounds having (potential) ionic groups and isocyanate-reactive groups. Examples thereof are recited in U.S. Pat. No. 3,479,310 and 4,056,564 and GB-1 455 554. Similarly, dihydroxyphosphonates, such as the sodium salt of ethyl 2,3-dihydroxypropanephosphonate, or the corresponding sodium salt of the unesterified phosphonic acid, can be used as ionic constructional component.

[0077] Preferred (potential) ionic monomers VI are N-alkyldialkanolamines, for example N-methyldiethanolamine, N-ethyldiethanolamine, diaminosulfonates, such as the sodium salt of N-(2-aminoethyl)-2-aminoethanesulfonic acid, dihydroxy-sulfonates, dihydroxycarboxylic acids such as dimethylolpropionic acid, diaminocarboxylic acid or -carboxylates such as lysine or the sodium salt of N-(2-aminoethyl)-2-aminoethanecarboxylic acid and diamines having at least one additional tertiary amine nitrogen atom, e.g., N-methyl-bis-(3-aminopropyl)amine.

[0078] Particular preference is given to diamino- and dihydroxycarboxylic acids, especially to the adduct of ethylenediamine with sodium acrylate or dimethylol-propionic acid.

[0079] Potential ionic groups initially introduced into the polyaddition product, if desired, are converted at least partly into ionic groups in a conventional manner by neutralization of the potential anionic or cationic groups or by quaternization of tertiary amine nitrogen atoms.

[0080] Potential anionic groups, for example carboxyl groups, are neutralized using inorganic and/or organic bases such as alkali metal hydroxides, carbonates or bicarbonates, ammonia or primary, secondary and particularly preferably tertiary amines such as triethylamine or dimethylaminopropanol.

[0081] To convert potential cationic groups, for example tertiary amine groups into the corresponding cations, for example ammonium groups, useful neutralizing agents include inorganic or organic acids, for example hydrochloric acid, phosphoric acid, formic acid, acetic acid, fumaric acid, maleic acid, lactic acid, tartaric acid or oxalic acid, and useful quaternizing agents include for example methyl chloride, methyl bromide, methyl iodide, dimethyl sulfate, benzyl chloride, ethyl chloroacetate or bromoacetamide. Further neutralizing or quaternizing agents are described for example in U.S. Pat. No. 3,479,310 at column 6.

[0082] This neutralization or quaternization of potential ionic groups can be effected before, during but preferably after the isocyanate polyaddition reaction.

[0083] The amounts of monomer VI (the degree of neutralization or quaternization being taken into account in the case of components containing potential ionic groups) is suitably chosen so that the polyurethanes contain from 0.05 to 2, preferably 0.07 to 1.0, particularly preferably from 0.1 to 0.7, meq of ionic groups/g of polyurethane.

[0084] Optionally, monofunctional amine or hydroxyl compounds are also used as constructional components (monomers VII). They are preferably monohydric polyether alcohols of the molecular weight range from 500 to 10 000 g/mol, preferably from 800 to 5 000 g/mol. Monohydric polyether alcohols are obtainable for example by alkoxylation of monohydric base molecules, for example methanol, ethanol or n-butanol, using ethylene oxide or mixtures of ethylene oxide with other alkylene oxides, particularly propylene oxide, as alkoxyating agents. When alkylene oxide mixtures are used, however, they preferably contain not less than 40, particularly preferably not less than 65, mol % of ethylene oxide.

[0085] Owing to monomer VII, the polyurethanes may thus optionally contain polyethylene oxide segments which are present in terminal polyether chains and which influence the hydrophilic character of the polyurethane as well as the ionic groups and ensure or improve dispersibility in water.

[0086] The compounds of the type mentioned, if used, are preferably used in such amounts that from 0 to 10%, preferably 0 to 5%, by weight of polyethylene oxide units are introduced by them into the polyurethane.

[0087] Further examples of compounds useful as monomers I to VII in the preparation of the polyurethanes described are described for example in High Polymers, Vol. XVI, "Polyurethanes, Chemistry and Technology", by Saunders-Frisch, Interscience Publishers, New York, London, Volume 1, 1962, pages 32 to 42 and pages 44 to 54 and Volume II, pages 5 to 6 and 198 to 199.

[0088] Useful monomers VIII, which in contrast to the above monomers contain ethylenically unsaturated groups, include for example esters of acrylic or methacrylic acid with polyols in which at least one OH group of the polyol remains unesterified. Of particular suitability are hydroxy-alkyl (meth)acrylates of the formula $\text{HO}(\text{CH}_2)_m\text{OOC}(\text{R}^{12})\text{C}=\text{CH}_2$ ($m=2$ to 8 ; $\text{R}^{12}=\text{H}$, CH_3) and their positional isomers, mono(meth)acrylic esters of polyetherdiols as recited for example under monomer II, trimethylolpropane mono- and di(meth)acrylate, pentaerythritol di- and tri(meth)acrylate or reaction products of epoxy compounds with (meth)acrylic acid as mentioned for example in U.S. Pat. No. 357 221. Of particular suitability are the adducts of (meth)acrylic acid with bisglycidyl ethers of diols such as, for example, bisphenol A or butanediol.

[0089] It is also possible to use adducts of (meth)acrylic acid with epoxidized diolefins, for example 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexanecarboxylate.

[0090] Incorporation of monomer VIII makes the polyurethane, if desired, thermally or photochemically postcurable in the presence or absence of an initiator.

[0091] The fraction of ethylenically unsaturated groups is generally below 0.2 mol per 100 g of polyurethane.

[0092] The total fraction of constructional components is preferably chosen in such a way that the sum total of isocyanate-reactive hydroxyl groups and primary or secondary amino groups is in the range from 0.9 to 1.2, particularly preferably from 0.95 to 1.1, based on 1 isocyanate group.

[0093] The preparation of the described polyurethanes, especially as dispersions, can be effected by customary methods as described for example in the above-cited references.

[0094] The polyurethane or, if a further reaction with amino-functional monomers IV or VI is intended, a polyurethane prepolymer still containing terminal isocyanate groups is preferably prepared in an inert water-miscible solvent, such as acetone, tetrahydrofuran, methyl ethyl ketone or N-methylpyrrolidone, from the monomers

[0095] I and II and optionally III, V, VI, VII and VIII, if VI contains no amino groups.

[0096] The reaction temperature is generally in the range from 20 to 160° C., preferably in the range from 50 to 100° C.

[0097] The reaction of the diisocyanates can be speeded up using customary catalysts, such as dibutyltin dilaurate, tin(II) octoate or diazabicyclo-(2,2,2)-octane.

[0098] The polyurethane prepolymer obtained can be further reacted with amino-functional compounds of monomers VI and optionally IV at 20 to 80° C., optionally after (further) dilution with solvents of the abovementioned kind, preferably with solvents having boiling points below 100° C.

[0099] The conversion of potential salt groups, for example carboxyl groups, or tertiary amino groups, which have been introduced into the polyurethane via monomer VI, into the corresponding ions is effected by neutralization with bases or acids or by quaternization of the tertiary amino groups before or during the dispersing of the polyurethane in water.

[0100] After dispersion, the organic solvent can be distilled off, if its boiling point is below that of water. Any higher-boiling solvents used can remain in the dispersion.

[0101] The polyurethane content of the dispersions can be in particular in the range from 5 to 70% by weight, preferably in the range from 20 to 50% by weight, based on the dispersions.

[0102] The dispersions may be additized with customary assistants, for example thickeners, thixotropicizers, oxidation and UV stabilizers or release agents.

[0103] Hydrophobic assistants, which may be difficult to disperse homogeneously in the finished dispersion, may also be added to the polyurethane or the prepolymer before dispersion, by the method described in U.S. Pat. No. 4,306, 998.

[0104] Use of hydrophilic modified polyisocyanates and polyurethanes

[0105] This invention also provides for the use of hydrophilic modified polyisocyanates (A) and polyurethanes (B)

in finishes for wrinkleproofing cellulosic textiles. Finishes are any liquid formulations which contain the hydrophilic modified polyisocyanate (A) and/or polyurethane (B) 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 in the form of an aqueous washing liquor or as a 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 hydrophilic modified polyisocyanate (A) and/or polyurethane (B) in the main wash cycle or after the main wash cycle in the refresher or rinse cycle of the washing machine.

[0106] The present invention also provides for the use of the hydrophilic modified polyisocyanate (A) and/or polyurethane (B) in the manufacture of textiles, textile treatment before and after laundering, in the main wash cycle, the laundry rinse cycle and ironing. Different formulations are needed in each case.

[0107] Textile treatment, conditioner and refresher formulations

[0108] The treatment before or after laundering may utilize a textile treatment which, as well as hydrophilic modified polyisocyanate (A) and/or polyurethane (B) in dissolved or dispersed form, contains a surfactant. In this treatment, the cellulosic textiles are for example sprayed with the hydrophilic modified polyisocyanate (A) and/or polyurethane (B) 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 hydrophilic modified polyisocyanate (A) and/or polyurethane (B) 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.

[0109] 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 hydrophilic modified polyisocyanate (A) and/or polyurethane (B) in dissolved or dispersed form according to the above-described process exhibit an excellent level of wrinkle and crease resistance that is durable to multiple laundering. There is frequently no longer any need to iron the textiles. The textiles thus treated additionally possess fiber and color protection.

[0110] The invention also provides a textile treatment comprising

[0111] a) from 0.1 to 40% by weight, preferably from 0.5 to 25% by weight, of at least one hydrophilic modified polyisocyanate (A) and/or at least one polyurethane (B),

[0112] b) from 0 to 30% by weight of silicones,

[0113] c) from 0 to 30% by weight of cationic and/or nonionic surfactants,

[0114] d) from 0 to 60% by weight of further ingredients such as further wetting agents, softeners, lubricants, water-soluble, film-forming and adhesive polymers, scents, dyes, stabilizers, fiber and color protection additives, viscosity modifiers, soil release additives, corrosion control additives, bactericides, preservatives and spraying assistants, and

[0115] e) from 0 to 99.9% by weight of water,

[0116] components a) to e) adding up to 100% by weight.

[0117] Preferred silicones are amino-containing silicones, which are preferably present in microemulsified form, alkoxyated, especially ethoxyated, silicones, polyalkylene oxide-polysiloxanes, polyalkylene oxide-aminopolydimethylsiloxanes, silicones having quaternary ammonium groups (silicone quats) and silicone surfactants.

[0118] Useful softeners or lubricants include for example oxidized polyethylenes 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.

[0119] A treatment formulation to be applied to the textile material by spraying may additionally include a spraying assistant. In some cases, it can also be of advantage to include in the formulation alcohols such as ethanol, isopropanol, ethylene glycol or propylene glycol. Further customary additives are scents, dyes, stabilizers, fiber and color protection additives, viscosity modifiers, soil release additives, corrosion control additives, bactericides and preservatives in customary amounts. 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.

[0120] The hydrophilic modified polyisocyanate (A) and/or the polyurethane (B) may also be used when the textiles are washed in the main wash cycle of the washing machine.

[0121] The invention further provides a solid laundry detergent formulation comprising

[0122] a) from 0.05 to 20% by weight of at least one hydrophilic modified polyisocyanate (A) and/or at least one polyurethane (B),

[0123] b) from 0.1 to 40% by weight of at least one nonionic and/or anionic surfactant,

[0124] c) from 0 to 50% by weight of an inorganic builder,

[0125] d) from 0 to 10% by weight of an organic cobuilder,

[0126] e) 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 polyesters, dyes, bactericides, dissolution improvers and/or disintegrants,

[0127] components a) to e) adding up to 100% by weight.

[0128] Useful anionic surfactants are in particular:

[0129] (fatty) alcohol sulfates of (fatty) alcohols having from 8 to 22, preferably from 10 to 18, carbon atoms, for example C₉- to C₁₁-alcohol sulfates, C₁₂- to C₁₄-alcohol sulfates, C₁₂- to C₁₈-alcohol sulfates, lauryl sulfate, cetyl sulfate, myristyl sulfate, palmityl sulfate, stearyl sulfate and tallow fatty alcohol sulfate;

[0130] sulfated alkoxyated C₈- to C₂₂-alcohols (alkyl ether sulfates). Compounds of this kind are prepared for example by first alkoxyating a C₈- to C₂₂-alcohol, preferably a C₁₀- to C₁₈-alcohol, for example a fatty alcohol, and then sulfating the alkoxylation product. The alkoxylation is preferably carried out using ethylene oxide;

[0131] linear C₈ to C₂₀-alkylbenzenesulfonates (LAS), preferably linear C₉- to C₁₃-alkylbenzenesulfonates and -alkyltoluenesulfonates,

[0132] alkanesulfonates such as C₈- to C₂₄-alkanesulfonates, preferably C₁₀- to C₁₈-alkanesulfonates

[0133] soaps such as, for example, the sodium and potassium salts of C₈- to C₂₄-carboxylic acids.

[0134] 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 hydroxyethyl ammonium, di(hydroxyethyl)ammonium and tri(hydroxyethyl)ammonium.

[0135] Useful nonionic surfactants are in particular:

[0136] alkoxyated C₈- to C₂₂-alcohols such as fatty alcohol alkoxyates or oxo alcohol alkoxyates. These may have been alkoxyated with ethylene oxide, propylene oxide and/or butylene oxide. Useful surfactants here include all alkoxyated 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 alkoxylation catalyst used to make them, alkoxyates have a broad or narrow alkylene oxide homolog distribution;

- [0137] alkylphenol alkoxyates such as alkylphenol ethoxyates having C₆- to C₁₄-alkyl chains and from 5 to 30 alkylene oxide units;
- [0138] alkylpolyglucosides 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, glucoside units;
- [0139] N-alkylglucamides, fatty acid amide alkoxyates, fatty acid alkanolamide alkoxyates and also block copolymers of ethylene oxide, propylene oxide and/or butylene oxide.
- [0140] Useful inorganic builders are in particular:
- [0141] crystalline or amorphous aluminosilicates having ion-exchanging properties such as zeolites in particular. Useful zeolites include in particular zeolites A, X, B, P, MAP and HS in their sodium form or in forms in which sodium has been partly replaced by other cations such as lithium, potassium, calcium, magnesium or ammonium;
- [0142] crystalline silicates such as in particular disilicates or sheet-silicates, for example δ -Na₂Si₂O₅ or β -Na₂Si₂O₅. Silicates can be used in the form of their alkali metal, alkaline earth metal or ammonium salts, preferably as sodium, lithium and magnesium silicates;
- [0143] amorphous silicates such as for example sodium metasilicate or amorphous disilicate;
- [0144] 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;
- [0145] polyphosphates such as for example pentasodium triphosphate.
- [0146] Useful organic cobuilders include in particular low molecular weight, oligomeric or polymeric carboxylic acids.
- [0147] Useful low molecular weight carboxylic acids include for example citric acid, hydrophobic 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, butanetetracarboxylic acid, cyclopentanetetracarboxylic acid, alkyl- and alkenylsuccinic acids and aminopolycarboxylic acids such as for example nitrilotriacetic acid, β -alaninediacetic acid, ethylenediaminetetraacetic acid, serinediacetic acid, isoserinediacetic acid, N-(2-hydroxyethyl)iminodiacetic acid, ethylenediaminedisuccinic acid and methyl- and ethylglycinediacetic acid;
- [0148] useful oligomeric or polymeric carboxylic acids include for example homopolymers of acrylic acid, oligomaleic acids, copolymers of maleic acid with acrylic acid, methacrylic acid, C₂-C₂₂-olefins such as for example isobutene or long-chain α -olefins, vinyl alkyl ethers having C₁-C₈-alkyl groups, vinyl acetate, vinyl propionate, (meth)acrylic esters of C₁- to C₈-alcohols and styrene. Preference is given to using the homopolymers of acrylic acid and copolymers of acrylic acid with maleic acid. Polyaspartic acids are also useful as organic cobuilders. Oligomeric and polymeric carboxylic acids are used in acid form or as sodium salt.
- [0149] A solid laundry detergent formulation according to the invention is customarily present in powder or granule form or in extrudate or tablet form.
- [0150] The invention further provides a liquid laundry detergent comprising
- [0151] a) from 0.05 to 20% by weight of at least one hydrophilic modified polyisocyanate (A) and/or at least one polyurethane (B),
- [0152] b) from 0.1 to 40% by weight of at least one nonionic and/or anionic surfactant,
- [0153] c) from 0 to 20% by weight of an inorganic builder,
- [0154] d) from 0 to 10% by weight of an organic cobuilder,
- [0155] e) 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, antiredeposition agents, soil release polyesters, dyes, bactericides, non-aqueous solvents, solubilizers, hydrotropes, thickeners and/or alkanolamines,
- [0156] f) from 0 to 99.85% by weight of water, components a) to f) adding up to 100% by weight.
- [0157] The abovementioned nonionic and anionic surfactants, builders and cobuilders may be used.
- [0158] A detailed description of the laundry detergent ingredients mentioned is found for example in WO 99/06524 or WO 99/04313 and in Liquid Detergents, Editor: Kuo-Yann Lai, Surfactant Sci. Ser., Vol. 67, Marcel Decker, New York, 1997, pp. 272-304.
- [0159] The concentration of the hydrophilic modified polyisocyanates or the polyurethanes in the wash liquor is for example in the range from 10 to 5 000 ppm, preferably in the range from 50 to 1 000 ppm. Textiles treated with the hydrophilic modified polyisocyanates or polyurethanes 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.
- [0160] The hydrophilic modified polyisocyanate (A) and/or polyurethane (B) may be used in the rinse or refresher cycle following the main wash cycle. The concentration of the hydrophilic modified polyisocyanates or the polyurethanes in the wash liquor is for example in the range from 10 to 5 000 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.

[0161] The invention also provides a laundry refresher comprising

[0162] a) from 0.05 to 40% by weight of at least one hydrophilic modified polyisocyanate (A) and/or at least one polyurethane (B),

[0163] b) from 0.1 to 40% by weight of a cationic surfactant,

[0164] c) from 0 to 30% by weight of a nonionic surfactant,

[0165] d) 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

[0166] e) from 0 to 99.85% by weight of water,

[0167] components a) to e) adding up to 100% by weight.

[0168] Preferred cationic surfactants are selected from the group of the quaternary diesterammonium salts, the quaternary tetraalkylammonium salts, the quaternary diamidoammonium salts, the amidoamine esters and imidazolium salts. Examples are quaternary diesterammonium salts which have two C_{11} - to C_{22} -alk(en)ylcarbonyloxy(mono- to pentamethylene) radicals and two C_1 - to C_3 -alkyl or -hydroxyalkyl radicals on the quaternary nitrogen atom and, for example, chloride, bromide, methosulfate or sulfate as counterion.

[0169] Quaternary diesterammonium salts further include in particular those which have a C_{11} - to C_{22} -alk(en)ylcarbonyloxytrimethylene radical bearing a C_{11} - to C_{22} -alk(en)ylcarbonyloxy radical on the central carbon atom of the trimethylene group and three C_1 - to C_3 -alkyl or -hydroxyalkyl radicals on the quaternary nitrogen atom and, for example, chloride, bromide, methosulfate or sulfate as counterion.

[0170] Quaternary tetraalkylammonium salts are in particular those which have two C_1 - to C_6 -alkyl radicals and two C_8 - to C_{24} -alk(en)yl radicals on the quaternary nitrogen atom and, for example, chloride, bromide, methosulfate or sulfate as counterion.

[0171] Quaternary diamidoammonium salts are in particular those which bear two C_8 - to C_{24} -alk(en)ylcarbonylaminoethylene radicals, a substituent selected from hydrogen, methyl, ethyl and polyoxyethylene having up to 5 oxyethylene units and as fourth radical a methyl group on the quaternary nitrogen atom and, for example, chloride, bromide, methosulfate or sulfate as counterion.

[0172] Amidoamino esters are in particular tertiary amines bearing a C_1 - to C_{22} -alk(en)ylcarbonylamino(mono- to trimethylene) radical, a C_{11} - to C_{22} -alk(en)ylcarbonyloxy(mono- to trimethylene) radical and a methyl group as substituents on the nitrogen atom.

[0173] Imidazolium salts are in particular those which bear a C_{14} - to C_{18} -alk(en)yl radical in position 2 of the heterocycle, a C_{14} - to C_{18} -alk(en)ylcarbonyl(oxy 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.

We claim:—

1. A process for wrinkleproofing cellulosic textiles by treating the textiles with a finish and drying the treated textiles, which said finish comprises (A) one or more hydrophilic modified polyisocyanates and/or (B) one or more polyurethanes in dissolved or dispersed form.

2. The use of hydrophilic modified polyisocyanates (A) and polyurethanes (B) in textile treatments, solid and liquid laundry detergents and laundry refreshers.

3. The use of finishes comprising at least one hydrophilic modified polyisocyanates (A) and/or at least one polyurethane (B) in textile manufacture, textile treatment, the laundry main wash cycle, the laundry rinse cycle and ironing.

4. A finish for wrinkleproofing cellulosic textiles, comprising at least one hydrophilic modified polyisocyanate (A) and at least one polyurethane (B).

5. A textile treatment comprising

a) from 0.1 to 40% by weight of at least one hydrophilic modified polyisocyanate (A) and/or at least one polyurethane (B),

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

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

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

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

6. A solid laundry detergent comprising

a) from 0.05 to 20% by weight of at least one hydrophilic modified polyisocyanate (A) and/or at least one polyurethane (B),

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

c) from 0 to 50% by weight of an inorganic builder,

d) from 0 to 10% by weight of an organic cobuilder,

e) 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 polyesters, dyes, bactericides, dissolution improvers and/or disintegrants,

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

7. A liquid laundry detergent comprising

- a) from 0.05 to 20% by weight of at least one hydrophilic modified polyisocyanate (A) and/or at least one polyurethane,
- b) from 0.1 to 40% by weight of at least one nonionic and/or anionic surfactant,
- c) from 0 to 20% by weight of an inorganic builder,
- d) from 0 to 10% by weight of an organic cobuilder,
- e) 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, antiredeposition agents, soil release polyesters, dyes, bactericides, nonaqueous solvents, solubilizers, hydrotropes, thickeners and/or alkanolamines,
- f) from 0 to 99.85% by weight of water, components a) to f) adding up to 100% by weight.

8. A laundry refresher comprising

- a) from 0.05 to 40% by weight of at least one hydrophilic modified polyisocyanate (A) and/or at least one polyurethane (B),
- b) from 0.1 to 50% by weight of at least one cationic surfactant,
- c) from 0 to 25% by weight of a nonionic surfactant,
- d) 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
- e) from 0 to 99.85% by weight of water, components a) to e) adding up to 100% by weight.

6. (New) A method of use of hydrophilic modified polyisocyanates (A) or polyurethanes (B) as wrinkleproofing agent in home textile treatments, comprising the step of treating a textile with the textile treatments before or after home laundering.

7. (New) The method of use as claimed in claim 6, wherein the textile treatment comprises

- a) from 0.1 to 40% by weight of at least one hydrophilic modified polyisocyanate (A) and/or at least one polyurethane (B),
- b) from 0 to 30% by weight of silicones,
- c) from 0 to 30% by weight of cationic and/or nonionic surfactants,
- d) from 0 to 60% by weight of further ingredients such as further wetting agents, softeners, lubricants, water-soluble, film-forming and adhesive polymers, scents, dyes, stabilizers, fiber and color protection additives, viscosity modifiers, soil release additives, corrosion control additives, bactericides, preservatives and spraying assistants, and
- e) from 0 to 99.9% by weight of water, the components adding up to 100% by weight.

8. (New) The method of use as claimed in claim 6, wherein the textile is treated during ironing.

9. (New) A method of use of hydrophilic modified polyisocyanates (A) and polyurethanes (B) as wrinkleproofing agent in a solid or liquid laundry detergents, comprising the step of washing a textile in the presence of the solid or liquid laundry detergent.

10. (New) The method of use as claimed in claim 9, wherein the solid laundry detergent comprises

- a) from 0.05 to 20% by weight of at least one hydrophilic modified polyisocyanate (A) and/or at least one polyurethane (B),
- b) from 0.1 to 40% by weight of at least one nonionic and/or anionic surfactant,
- c) from 0 to 50% by weight of an inorganic builder,
- d) from 0 to 10% by weight of an organic cobuilder,
- e) 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 polyesters, dyes, bactericides, dissolution improvers and/or disintegrants,

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

11. (New) The method of use as claimed in claim 9, wherein the liquid laundry detergent comprises

- a) from 0.05 to 20% by weight of at least one hydrophilic modified polyisocyanate (A) and/or at least one polyurethane (B),
- b) from 0.1 to 40% by weight of at least one nonionic and/or anionic surfactant,
- c) from 0 to 20% by weight of an inorganic builder,
- d) from 0 to 10% by weight of an organic cobuilder,
- e) 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, antiredeposition agents, soil release polyesters, dyes, bactericides, nonaqueous solvents, solubilizers, hydrotropes, thickeners and/or alkanolamines,
- f) from 0 to 99.85% by weight of water, components a) to f) adding up to 100% by weight.

12. (New) The method of use as claimed in claim 9, wherein the solid or liquid laundry detergent is present in the main wash cycle of a washing machine.

13. (New) A method of use of hydrophilic modified polyisocyanates (A) or polyurethanes (B) as wrinkleproofing agent in laundry refreshers, comprising the step of rinsing a textile with a rinse liquor containing the laundry refresher.

14. (New) The method of use as claimed in claim 13, wherein the laundry refresher comprises

- a) from 0.05 to 40% by weight of at least one hydrophilic modified polyisocyanate (A) and/or at least one polyurethane (B),
- b) from 0.1 to 50% by weight of at least one cationic surfactant,
- c) from 0 to 25% by weight of a nonionic surfactant,

d) 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

e) from 0 to 99.85% by weight of water, components a) to e) adding up to 100% by weight.

15. (new) The method of use as claimed in claim 13, wherein the laundry refresher is present in the rinse or refresher cycle of a washing machine following the main wash cycle.

16. (New) A solid laundry detergent comprising

a) from 0.05 to 20% by weight of at least one hydrophilic modified polyisocyanate (A) and/or at least one polyurethane (B),

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

c) from 0 to 50% by weight of an inorganic builder,

d) from 0 to 10% by weight of an organic cobuilder,

e) 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 polyesters, dyes, bactericides, dissolution improvers and/or disintegrants, components a) to e) adding up to 100% by weight.

17. (New) A liquid laundry detergent comprising

a) from 0.05 to 20% by weight of at least one hydrophilic modified polyisocyanate (A) and/or at least one polyurethane (B),

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

c) from 0 to 20% by weight of an inorganic builder,

d) from 0 to 10% by weight of an organic cobuilder,

e) 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, antiredeposition agents, soil release polyesters, dyes, bactericides, nonaqueous solvents, solubilizers, hydrotropes, thickeners and/or alkanolamines,

f) from 0 to 99.85% by weight of water, components a) to f) adding up to 100% by weight.

18. (New) A laundry refresher comprising

a) from 0.05 to 40% by weight of at least one hydrophilic modified polyisocyanate (A) and/or at least one polyurethane (B),

b) from 0.1 to 50% by weight of at least one cationic surfactant,

c) from 0 to 25% by weight of a nonionic surfactant,

d) 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

e) from 0 to 99.85% by weight of water, components a) to e) adding up to 100% by weight.

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