

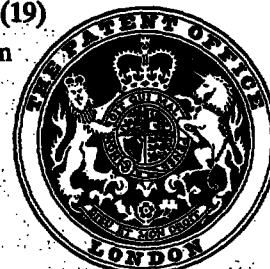
PATENT SPECIFICATION

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- (21) Application No. 47438/77 (22) Filed 15 Nov. 1977 (19)
 (31) Convention Application No. 14465/76 (32) Filed 17 Nov. 1976 in
 (33) Switzerland (CH)
 (44) Complete Specification Published 4 Feb. 1981
 (51) INT. CL.³ C08G 18/28
 D06M 15/00
 D06P 1/52 1/60 1/607



- (52) Index at Acceptance
 C3R 32D17 32D6A 32D6D 32D6G 32D6H
 32D6I 32D6K 32G2X 32G2Y 32G3A
 32G4 32J10 32J1A 32J1X 32J1Y
 32J2C 32J2E 32J2F 32J3Y
 32J5 32J7Y 32KB 32KH 32KL 33C
 33P C12 C13M C13S C14B C16 C21
 C4 C6X L1B L2X L5C L5D L6H
 C3Y B230 B240 B243 B310 B312 F210
 F510
 C5F 134 316 401 410 501 61Y 632 749
 809 B MA
 D1B 2L13 2L15 2L1B 2L29A 2L2A 2L30A
 2L3 2L5A 2L5D2 2L5D 2L9
 D1P 1270 1302 1316 1317 1318 DP

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(54) WATER-SOLUBLE OR -DISPERSIBLE POLYURETHANES AND THEIR USE IN A WET-TREATMENT PROCESS FOR TEXTILE MATERIALS

(71) We, SANDOZ LTD., of 35 Lichtstrasse, 4002 Basle, Switzerland, a Swiss Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

In the wet processing of synthetic or semi-synthetic textile materials by modern processing methods, especially in winch-beck and jet dyeing machines, the undesirable formation of creases in the material represents a problem. Such crease formation, for example, can lead to unlevel dyeing.

It has now been discovered that the tendency of the material to creasing can be considerably reduced or even eliminated if the wet processing is effected in the presence of certain water-soluble or -dispersible polyurethanes having the property of increasing the fibre/fibre lubricity and which can be named lubricating agents.

The present invention relates to such lubricating agents and their use in the wet processing of textile materials, and, more particularly, provides a wet treatment process for synthetic or semi-synthetic textile material comprising treating the textile material with a liquor containing a polyurethane, which polyurethane is a reaction product of a compound or mixture of compounds 1, the or each compound 1 being a derivative of ammonia; a polyamine; urea; a polyamide; an aminoamide; an aminoalcohol; or a polyol containing up to 10 carbon atoms and up to 6 hydroxyl groups per molecule; in which at least three of the active hydrogen atoms of the amino, hydroxyl and/or amido moieties present are replaced by the same or different groups of formula 1a,



1a

in which each Alkylene, independently, is straight or branched chain (C_{2-4})-alkylene, unsubstituted or substituted by a phenyl group, and n is an integer 1 to 100, and a compound or mixture of compounds 2, the or each compound 2 being a hydrocarbon polyisocyanate, in a molar ratio of compound 1 : compound 2 of $\Sigma p : \Sigma r$, p being the number of moles of each compound 1 and r being the number of moles of each compound 2 reacted, Σp and Σr being so chosen that $\Sigma(p.q) + \Sigma(r.m) = 1.5$ to 21 and $\Sigma p \leq \Sigma(r.m)$, q

being the number of groups of formula 1a per molecule of each compound 1 and m being the number of isocyanate groups per molecule of each compound 2, and which polyurethane is water-soluble or -dispersible to a degree of at least 1 g/l at 20°C, and whose 1 g/l aqueous solution or dispersion at 20°C exhibits a viscosity of no more than 100 cp.

Thus the relative amounts of the reacting species used to produce the polyurethane employed in the process of the present invention is such that the total number of molecules of compound 1 does not exceed the total number of NCO groups in the compound 2, and that the polyurethane reaction product has a ratio of free hydroxyl groups present in groups of formula 1a: urethane groups of from 0.5:1 to 20:1, it preferably being from 0.5:1 to 10:1, preferably in the upper region of said latter range when the product is of relatively high molecular weight.

By the expression "water-dispersibility of at least 1 g/l at 20°C" used above is meant that displayed when an aqueous dispersion of the polyurethane product containing at least 1 g/l of the product remains stable, i.e. does not show any visible signs of deposition of the dispersed product, after standing at 20°C for at least 12 hours.

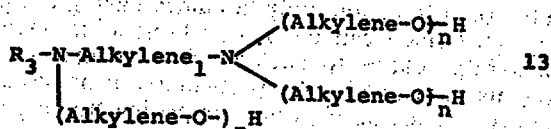
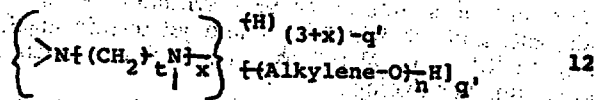
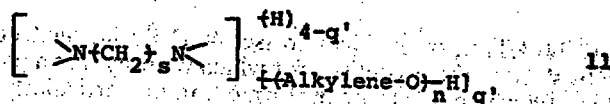
Preferably the polyurethane product is water-soluble rather than merely water-dispersible, and has a water-solubility of at least 10 g/l, more preferably at least 25 g/l, at 20°C.

The melting point of the polyurethanes used in the process of the present invention preferably does not exceed 150°C.

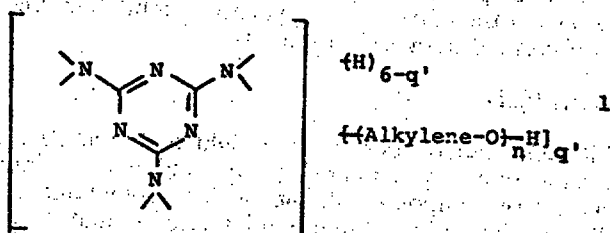
The polyurethane products may still contain a certain amount of untreated free isocyanate groups, but for the purposes of the present invention, up to 1% of the unreacted isocyanate groups originally present in the starting compound 2 in the product can be tolerated.

In the compounds 1, there are preferably present at least as many alkyleneoxy units as the number of active amino, hydroxy and/or amide hydrogen atoms in the original ammonia, polyamine, urea, polyamide, aminoamide, aminoalcohol or polyol.

When the compound 1 is a polyoxyalkylated polyamine, this compound preferably contains 2 to 6 nitrogen atoms per molecule, and more preferably is selected from the polyoxyalkylated aliphatic polyamines of formulae 11, 12 and 13,



and from polyoxyalkylated melamine of formula 14,



in which s is an integer 2 to 6,
each t, independently, is an integer 2 or 3,
x is an integer 2, 3 or 4,
R₃ is (C₁₋₃₀)alkyl or (C₃₋₂₀)alkenyl.

Alkylene₁ is (CH₂)₂, (CH₂)₃ or (CH₂)₄,

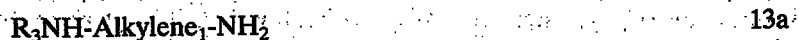
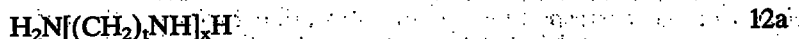
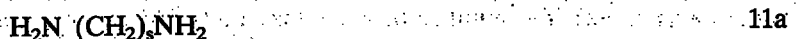
q' is an integer at least 3, its maximum values being 4, (3+x) and 6 for the compounds of formula 11, 12 and 14, respectively, and each Alkylene, independently, and n, independently, are as defined above.

In the formula 11, s is preferably 2 or 3.

Alkylene₁ in the formula 13 is preferably (CH₂)₂ or (CH₂)₃. R₃ in this formula, independently of any preferred meaning for Alkylene₁, is preferably an alkyl or alkenyl group containing at least 8 carbon atoms, more preferably a (C₈₋₂₄)alkyl or (C₈₋₂₀)alkenyl group. Most preferably, R₃ is lauryl, myristyl, palmityl, stearyl, arachidyl, behenyl or oleyl.

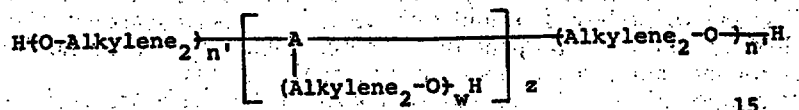
The preferred polyoxyalkylated polyamines are those of formulae 11, 12 and 13.

When the compound 1 is a polyoxyalkylated polyamide, the polyamide from which it is derived preferably has an average molecular weight in the range 500-30,000, i.e. is a higher molecular weight polyamide. Such polyamides can be aliphatic, aromatic or araliphatic, any aliphatic unit preferably containing 1 to 36, more preferably 4 to 12, carbon atoms, any aromatic unit preferably being C₆₋₁₀ and being derived from benzene or naphthalene, and any araliphatic unit preferably containing 7 to 25 carbon atoms, the aromatic units therein preferably being derived from benzene and/or naphthalene. Preferably the polyoxyalkylated polyamide is derived from a conventionally employed alcohol-soluble nylon with a melting point between 50 and 160°C, more preferably from those which are themselves derived from dimerised (C₁₀₋₂₀) unsaturated fatty acids and di- or polyamines. Preferably the di- or polyamines employed in the production of such polyamides are selected from the compounds of formulae 11a, 12a and 13a

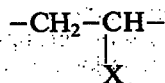


in which s, each t independently, x, R₃ and Alkylene₁ are as defined above.

In general, the polyoxalated polyamides from which the polyurethanes used in the process of the present invention are produced preferably conform to the formula 15,



in which A is a repeating unit of an aliphatic, aromatic or araliphatic polyamide, the bond to (Alkylene₂-O)_wH being from the nitrogen atom or a -CON- or -CONH moiety contained in the repeating unit, each Alkylene₂, independently, is a divalent group of formula,

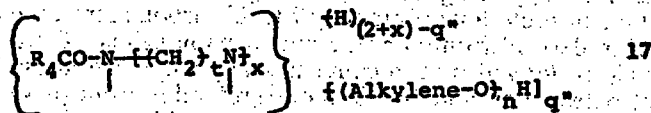
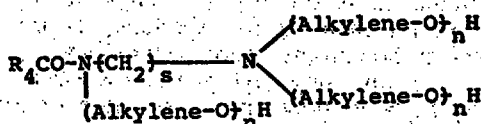


wherein X is a hydrogen, methyl, ethyl or phenyl,

each n, independently, is an integer 3 to 30, each w, independently, is 0 or an integer of 3 to 30, and z is an integer 5 to 1000, each repeating unit A being the same or different, at least three of the active hydrogen atoms of the amido moieties of the pre-oxyalkylation precursor thereof being replaced by the same or different groups (Alkylene₂-O)_nH, and in which the number of (Alkylene₂-O) units present is at least as great as the number of active hydrogen atoms in the amido moieties of the pre-oxyalkylation precursor.

Of the compounds of formula 15, those in which any Alkylene₂ moiety is ethylene-1,2 or propylene-1,2 are preferred.

When the compound 1 is a polyoxyalkylated aminoamide, this is preferably a polyoxyalkylated amidation product of an aliphatic monocarboxylic acid or of a functional derivative thereof, e.g. its acid chloride, acid bromide, anhydride or an ester, and one or more polyamines of formulae 11a and 12a, as defined above. Such polyoxyalkylated amidation products are preferably those of formulae 16 and 17,



in which R_4 is (C_{1-23}) alkyl or (C_{2-19}) alkenyl, s , each t , independently, x , and each Alkylene and each n , independently, are as defined above, and q'' is an integer at least 3, its maximum value being $(2+x)$, the number of alkeneoxy units present in a compound of formula 17 being at least as great as the number of active hydrogen atoms in the amino and amido moieties of the corresponding pre-oxyalkylation precursor thereof.

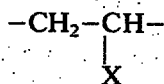
In both formulae 16 and 17, R_4CO is preferably (C_{8-24}) alkanoyl, more preferably (C_{12-22}) alkanoyl, or (C_{8-20}) alkenoyl. Most preferably R_4CO is derived from lauric, myristic, palmitic, stearic, arachic, behenic, oleic, linoleic or linolenic acid. s in the formula 16 is preferably 2 or 3.

When the compound 1 is a polyoxyalkylated aminoalcohol, this is preferably a polyoxyalkylated derivative of an alkanolamine containing a single amino group and 1 to 3 hydroxyl groups per molecule, more preferably one containing 4 to 6 carbon atoms per molecule. Particularly preferred examples of these are the polyoxyalkylated derivatives of 2-amino-2-hydroxymethyl-1,3-propane diol, 2-amino-2-methyl-1,3-propane diol, 2-amino-2-ethyl-1,3-propane diol and 2-amino-2-hydroxymethyl-propane.

When the compound 1 is a polyoxyalkylated polyol, this is preferably a polyoxyalkylated derivative of an aliphatic polyol containing 3 to 10 carbon atoms and 3 to 6 hydroxyl groups per molecule. Particularly preferred examples of these are the polyoxyalkylated derivatives of glycerol, 1,1,1-trimethylolpropane, 1,2,4-trihydroxybutane, pentaerythritol, sorbitol, mannitol and tetramethylolcyclohexanol.

In general the compound 1 preferably contains no aromatic or unsaturated aliphatic radicals emanating from the precursor before polyoxyalkylation. It is preferably a polyoxyalkylated derivative of ammonia, of a polyamide, or of any of the remaining active hydrogen atom-containing precursors in which 3 to 7, more preferably 3 to 5, or most preferably 3, of the active hydrogen atoms are replaced by one or more groups of formula 1a, as defined above. More preferably the compound 1 is a polyoxyalkylated derivative of ammonia; a polyamide; or a polyamine, aminoamide, aminoalcohol or polyol in which 3 to 7, more preferably 3 to 5, or most preferably 3, of the active hydrogen atoms are replaced by one or more groups of formula 1a. Most preferably the compound 1 is a polyoxyalkylated derivative of ammonia.

Alkylene in the formula 1a is preferably Alkylene₂, i.e. a divalent group of formula



in which X is hydrogen, methyl, ethyl or phenyl, or more preferably ethylene-1,2 or propylene-1,2, i.e. of the above formula, in which X is hydrogen or methyl.

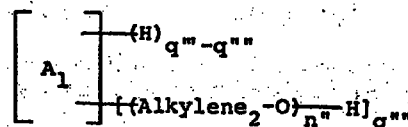
In all the compounds 1 except the polyoxyalkylated derivatives of ammonia and of a polyamide, preferably 3 to 7, more preferably 3 to 5, or most preferably 3 of the active hydrogens of the active hydrogen atom-containing precursors of the polyoxyalkylated derivatives are replaced by one or more groups of formula 1a, as defined above.

n is preferably an integer 3 to 50, or more preferably 3 to 30, except in the case where the compound 1 is a polyalkoxylated derivative of ammonia, in which case n is preferably 3 to

100. When the active hydrogen-containing precursor of the compound 1 contains two or more nitrogen atoms, n is even more preferably 3 to 20.

Preferably the compound 1 is such that a 5% aqueous solution thereof has a pH of 4 to 12, more preferably 6 to 8.

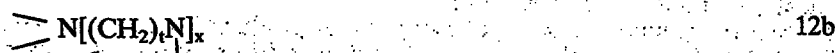
A preferred group of compounds 1 for use in the process of the present invention is thus constituted by the compounds of formula 1',



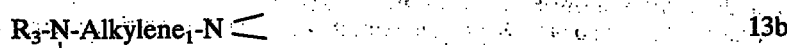
in which A₁ is nitrogen,
a radical 11b,



a radical 12b,



a radical 13b,



a radical of an aliphatic, aromatic or araliphatic polyamide containing 5 to 1000 repeating units, said radical being derived from the polyamide by removal of the hydrogen atoms from the -CONH₂ and -CONH- groups,

a radical 16b,



a radical 17b,



a radical of an alkanolamine containing a single amino group, 1 to 3 hydroxyl groups and 4 to 6 carbon atoms per molecule, said radical being derived from the alkanolamine by removal of the hydrogen atoms from the amino and from the hydroxyl group or groups, or a radical of an aliphatic polyol containing 3 to 10 carbon atoms and 3 to 6 hydroxyl groups per molecule, said radical being derived from the polyol by removal of the hydrogen atoms from the hydroxyl groups,

s, each t, independently, x, R₃, Alkylene₁, R₄ and each Alkylene₂, independently, are as defined above,

each n'', independently, is, when A₁ is nitrogen, an integer 3 to 100, or, when A₁ is any other of the indicated radicals, an integer 3 to 30,

q''' is the maximum valency for each radical signified by A₁, being 3 when A₁ is nitrogen, 4 when A₁ is a radical 11b, (3+x) when A₁ is a radical 12b, 3 when A₁ is a radical 13b, 7 to 1002 when A₁ is a radical of a polyamide containing 5 to 1000 repeating units, respectively, 3, 4 or 5 when A₁ is a radical of an alkanolamine containing 1, 2 or 3 hydroxyl groups per molecule, respectively, or 3, 4, 5 or 6 when A₁ is a radical of an aliphatic polyol containing 3, 4, 5 or 6 hydroxyl groups, respectively,

and q''' is an integer 3 to q''',

with the proviso that when A₁ is a polyamide radical, the polymeric chain of the polyoxyalkylated polyamide is terminated at both ends by a group [(Alkylene₂-O)_nH]_{q'''}, and each repeating unit is the same or different, and the number of (Alkylene₂-O) units present is at least as great as the number of active hydrogen atoms in the amido moieties of the pre-oxyalkylation precursor.

In the compounds of formula 1', each Alkylene₂, independently, is preferably

ethylene-1,2 or propylene-1,2...n", when A_1 contains 2 or more nitrogen atoms, is preferably 3 to 20. Except when A_1 is a polyamide radical, g''' is preferably 3 to 5 when the values 4 or 5 are possible.

Amongst the preferred group of compounds of formula 1' are the compounds of formula 15, as defined above, which correspond with the compounds of formula 1', in which A_1 is a radical of a polyamide containing 5 to 1000 repeating units.

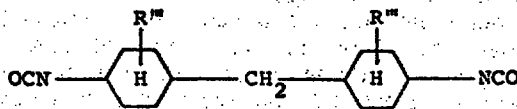
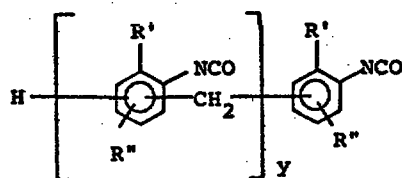
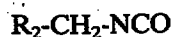
Of the compounds of formula 1', those in which A_1 is nitrogen or a radical of a polyamide, of an alkanolamine or of an aliphatic polyol are preferred, especially those in which A_1 is nitrogen.

Preferably at least 35 mol %, more preferably at least 50 mol %, or most preferably all, of the Alkylene or Alkylene₂ moieties in the compounds 1 and of formulae 15 and 1' are ethylene groups.

Any hydrocarbon polyisocyanate can be used as a compound 2 for production of the polyurethanes used in the process of the present invention, especially those hydrocarbon polyisocyanates conventionally used as starting materials in the production of polyurethanes. The hydrocarbon moiety can be aliphatic, aromatic or araliphatic, any aliphatic group being straight or branched chain, saturated or unsaturated. For the purposes of this specification, the term "aliphatic", when applied to aliphatic or araliphatic polyisocyanates, includes "alicyclic" as well as "acyclic". The hydrocarbon polyisocyanate preferably has 2 to 12 isocyanato substituents, most preferably 2 to 6, even more preferably 2 to 4 or most preferably 2, per molecule.

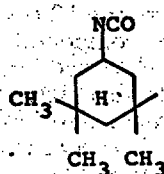
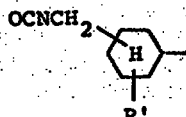
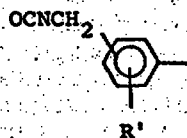
Preferably the compounds 2 are polyisocyanates produced from reaction of the corresponding polyamines with phosgene or of acid anhydrides or olefins with isocyanic acid, from Curtius rearrangement of the corresponding acylazides or from reaction of nitro compounds with carbon monoxide in known manner.

More preferably the hydrocarbon polyisocyanates 2 are selected from those of formulae 21, 22, 23 and 24:



in which R_1 is straight or branched chain (C_{2-40}) alkylene; cyclohexylene, saturated or unsaturated with one or two double bonds and unsubstituted or substituted with 1 to 3 (C_{1-2}) alkyl groups; or phenylene, diphenylene or naphthylene, each unsubstituted or substituted with 1 or 2 (C_{1-9}) alkyl groups, the -NCO groups on diphenylene being on different benzene nuclei,

R_2 is a radical of formula,



each R' , independently, is hydrogen or (C_{1-9}) alkyl,
each R'' , independently, is hydrogen or $-\text{NCO}$,
each R''' , independently, is hydrogen or methyl,
and y is an integer 1 to 5,

there being no more than 6 $-\text{NCO}$ groups per molecule, and any two $-\text{NCO}$ groups on the same benzene ring being *m*- or *p*- to each other, in the compounds of formula 23.

When R_1 in formula 21 is alkylene, this is preferably (C_{2-34}) , or more preferably (C_{2-6}) alkylene. When it is (C_{1-2}) alkyl-substituted cyclohexylene, any alkyl substituent is preferably methyl.

Any (C_{1-9}) alkyl substituent on phenylene, diphenylene or naphthylene, when R_1 signifies alkyl-substituted phenylene, diphenylene or naphthylene, respectively, is preferably (C_{1-3}) alkyl, more preferably (C_{1-2}) alkyl, or most preferably methyl. Similarly, the (C_{1-9}) alkyl radical signified by any R' is preferably (C_{1-3}) alkyl, more preferably (C_{1-2}) alkyl, or most preferably methyl.

y in the formula 23 is preferably 1 to 3, or more preferably 1 or 2.

Especially preferred compounds 2 are 1,2-dimethylene-diisocyanate, 1,6-hexamethylenediisocyanate and further α,ω -polymethylene diisocyanates containing up to 34 carbon atoms in the polymethylene chain, isophoron diisocyanate, xylylene diisocyanate, 1,3-bis(isocyanatomethyl) cyclohexane, cyclohexylene diisocyanate, 2,4- and 2,6-tolylene diisocyanate, *m*-phenylene diisocyanate, xylene diisocyanate, 1,5-naphthylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-diphenylene diisocyanate, 3,3'-dimethyl-4,4'-diisocyanatodiphenylmethane and polymethylene polyphenylene isocyanates (compounds of formula 23), e.g. such isocyanates produced as reaction products from phosgene with aniline-formaldehyde condensates.

The most preferred compounds 2 are selected from hexamethylenediisocyanate, 2,4- and 2,6-tolylene diisocyanates and polymethylene polyphenylene isocyanates containing 2 to 4 isocyanate groups per molecule, of which the aliphatic isocyanates are preferred to the aromatic ones.

The reaction between compound 1 and compound 2 can be effected under acid, neutral or basic conditions, preferably under slightly acid conditions. Depending on the pH value of the reaction mixture, it may or may not be necessary or desirable to acidify or basify the mixture by conventional manner to create favourable pH conditions for reaction. Furthermore, the reaction can be effected under anhydrous or practically anhydrous conditions, suitably by mere admixture of the reagents in the above mentioned molar ratio and heating, preferably between 70 and 150°C, more preferably between 80 and 130°C.

Alternatively the reaction can be effected in the presence of an organic solvent. Suitable organic solvents are polar solvents which contain no reactive hydrogen atoms capable of participating in the reaction with either of the reagents, and are preferably selected from acetone, dimethyl formamide and dioxan.

Preferably the reaction is carried out in the absence of a solvent.

The relative molar quantities of the reagents are preferably such as to result in a product having a ratio of free hydroxyl groups to urethane groups of from 0.5:1 to 10:1. Where the product is to be of relatively high molecular weight, this ratio is preferably in the upper region of the given range.

As is conventional in polyurethanes production, isocyanate 2 can be used in the reaction in partially or fully blocked form instead of in the form in which the isocyanate groups are free. When used in blocked form, the unblocked form is generated *in situ* under the reaction conditions, such that the free isocyanate groups become available for reaction with the hydroxyl groups of compound 1. By the expression "blocked form" is meant in a form in which some or all of the isocyanate groups have been converted to polyurethane groups, these being labile under the reaction conditions used for reacting compound 1 with compound 2.

Preferably the blocked isocyanates 2 have been blocked, partially or fully, with a phenol, preferably toluol or unsubstituted phenol and/or with a readily removable aliphatic alcohol, e.g. 1,1,1-tris(hydroxymethyl)ethane or -propane, and preferably the blocking is such that no free hydroxyl groups emanating from the blocking agent are present in the blocked isocyanate.

As is also conventional, when a compound 2 is used in partially or fully blocked form in the reaction between compound 1 and compound 2, the reaction must be conducted at or above the temperature at which the unblocked form of compound 2 is generated from the blocked form, more preferably at somewhat higher temperatures. Preferably the reaction is conducted within the temperature range 100-150°C, more preferably 110-130°C.

In all cases the reagents are generally first contacted with each other at a relatively low temperature e.g. at about 60°C, and then the mixture is heated to the suitable reaction temperature and maintained at this temperature until the desired degree of reaction has occurred, i.e. until the reaction product is practically free of isocyanate groups. Generally the reaction is sufficient when there remains 1% or less of the isocyanate groups originally present in the starting compound 2. The course of the reaction can be followed by periodically testing samples of the reaction mixture in known manner, e.g. to determine the extent to which unreacted isocyanate groups are present in the reaction mixture or from viscosity measurements. Completion of reaction is signified when no more, or practically no more, free isocyanate groups of compound 2 are available for reaction with the hydroxyl groups of compound 1. Completion of the reaction may also often be recognized by the commencement of gelatinization of the reaction mixture.

The present invention further provides new compounds within the scope of the polyurethanes used in the process of the present invention, which are polyurethane products of the reaction between a compound or a mixture of compounds of formula 1', as defined above, and a compound or mixture of compounds 2, as also defined above, in a molar ratio of compound of formula 1' : compound 2 of $\Sigma p' : \Sigma r'$, p' being the number of moles of each compound of formula 1' and r' being the number of moles of each compound 2 reacted, and $\Sigma p'$ and $\Sigma r'$ being so chosen that $\Sigma(p' \cdot q''') \div \Sigma(r' \cdot m) = 1.5$ to 21 and $\Sigma p' \leq \Sigma(r' \cdot m)$, q''' being the number of groups of formula 1'a,



1'a

per molecule of each compound of formula 1' and m being the number of isocyanate groups per molecule of each compound 2, and which polyurethane products are water-soluble or dispersible to a degree of at least 1 g/l at 20°C, and whose 1 g/l aqueous solution or dispersion at 20°C exhibits a viscosity of no more than 100 cp.

Thus the relative amounts of the reacting species used to produce the polyurethanes of the present invention is such that the total number of molecules of compound of formula 1' does not exceed the total number of -NCO groups in compound 2, and that the polyurethane reaction products have a ratio of free hydroxyl groups : urethane groups of from 0.5:1 to 20:1.

The afore-mentioned preferences for the polyurethanes used in the process of the present invention and for the starting materials used in their production, i.e. the compounds 1 and 2, apply also to the polyurethanes of the present invention and to the starting materials used in their production, i.e. the compounds of formula 1' and the compounds 2, respectively. The polyurethanes of the present invention are producible under the reaction conditions indicated above for producing the polyurethanes in general used in the process of the present invention.

The compounds 1, e.g. of formula 1', are either known or can be produced by conventional methods, preferably by oxyalkylation of the preoxyalkylation precursors of the compounds 1. In the case of the compounds 1 which are polyoxyalkylated derivatives of ammonia, such compounds are preferably produced by oxyalkylation of appropriate mono-, di- or tri-alkanolamines with the appropriate alkylene oxide or halohydrin, or with appropriate polyalkyleneoxy compounds, preferably with an average molecular weight of 100 to 6000, in conventional manner.

The compounds 2 are either known, or can be produced by methods analogous to the

known methods, e.g. as indicated hereinbefore.

The process of the present invention can be effected simultaneously with any wet treatment process for synthetic or semi-synthetic textile materials, e.g. dyeing, optical brightening, bleaching, washing, boiling and fixation, i.e. generally any wet treatment process in which the treated textile material tends to crease during treatment in an aqueous bath. Preferably the process is effected simultaneously with a dyeing process, especially in a winch-beck or jet dyeing machine. Here the difference between a textile material dyed in the absence of the lubricating agent and one dyed in its presence is often clearly visible, signs of the creasing, e.g. a streaky appearance, in the first case being largely or totally absent in the second case.

Preferred synthetic or semi-synthetic textile materials treated by the process of the present invention are of cellulose 2½ acetate, cellulose triacetate, polyamide, polyester and/or polyacrylonitrile, of which polyamide materials are most preferably treated.

When the wet treatment process is a dyeing process, any dyestuff may be used together with the polyurethane lubricating agent in the treatment liquor, its/nature depending, *inter alia*, on the dyeing method employed and on the substrate to be dyed. Examples of the dyestuffs employable are anionic, metal complex, disperse and basic dyestuffs, e.g. those listed in the Color Index under "Acid Dyes", "Mordant Dyes", "Disperse Dyes" and "Basic Dyes". The process of the present invention is preferably, however, effected in dyeing processes with anionic or disperse dyestuffs, more preferably with disperse dyestuffs, in which the polyurethane lubricating agents display especially good effects.

The polyurethane lubricating agents are preferably present in the wet treatment liquor employed at temperatures between 50 and 150°C, and, independently, at a concentration between 0.1 and 5 g, more preferably 0.3 to 1 g, of polyurethane reaction product (active substance) per litre of treatment liquor.

After the wet treatment process, the polyurethane lubricating agents used are washed out of the treated textile material in the usual washing and/or rinsing operations.

The polyurethane lubricating agents used in the process of the present invention do not significantly adversely affect the action of the dyestuff or other treatment agent used simultaneously or the treated textile material. For example, the light, wet and rubbing fastnesses of dyeings and the migratory properties of the dyestuffs in or on the substrates are not significantly adversely affected.

The polyurethane lubricating agents are preferably added to the treatment liquor before the wet treatment process is begun in the form of an aqueous concentrate. Such concentrates preferably contain at least 25% by weight of polyurethane reaction product (active substance), or more preferably at least 50% by weight. The viscosity of such aqueous concentrates preferably does not exceed 100,000 cp at 20°C.

Alternatively, the concentrate may be diluted with water before addition to the treatment liquor.

The present invention further provides aqueous concentrates of the compounds of the present invention, as defined hereinbefore, preferably at a concentration at least 25 %, or more preferably at a concentration at least 50% by weight.

The invention is illustrated by the following Examples, in which temperatures are given in degrees Centigrade. Examples 1 to 25 illustrate the production of the polyurethane lubricating agents for use in the process of the present invention, and the "Application Examples" illustrate the process.

The products of Examples 1 to 25 are water-soluble or -dispersible to a degree of at least 1 g/l at 20°C and their 1 g/l aqueous solutions or dispersions have a viscosity of no more than 100 cp at 20°C.

Example 1.

200 g of a polyamide with an acid number of 5.6 and a base number of 5.41 (expressed as mg KOH.g⁻¹) are melted at 130° in a current of nitrogen, and then 2 g of powdered sodium hydroxide are added. The nitrogen current is stopped and ethylene oxide is introduced with vigorous stirring at a speed at which full reaction ensues. After 10 hours, 475 g of ethylene oxide are added to the polyamide, and after the reactor has been rinsed with nitrogen, the slightly brown reaction product (I) is cooled and discharged. Titration of (I) gives an equivalent weight of 410 g per hydroxyl group.

3.5 g of hexamethylene diisocyanate are added dropwise over the course of 30 minutes at 45° with stirring to 50 g of (I) which has been slightly acidified with 100% sulphuric acid (pH value 6.5 with a 5% aqueous solution) and the mixture is reacted for 30 minutes. The reaction mixture is then heated to 100° and stirred for 2 more hours. As the viscosity of the oligomer begins to increase, 214 g of cold water are added, and the mixture is stirred until a solution (II) is produced. At 20°, (II) has a viscosity of 2,500 cp.

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Example 2

100 g of (I) are neutralised (pH 7.0 with a 5% aqueous solution) with sulphuric acid by the same process as described in Example 1 and are treated with 5 g of tolylene diisocyanate (80% 2,4- and 20% 2,6-isomer) for one hour at 115°. After dissolving the reaction mixture in 307 g of distilled water, a solution (III) is obtained, which has a viscosity of 750 cp.

Example 3

100 g of (I) are reacted by the same process as described in Example 2 with a mixture of 3 g of hexamethylene diisocyanate and 4 g of tolylene diisocyanate for 10 hours. A 25% aqueous solution (IV) of the end-product has a viscosity of 850 cp.

Example 4

100 g of (I) are reacted by the same process as described in Example 1 with 3.5 g of a polymethylene polyphenylene isocyanate (139 g/equivalent, functionality related to NCO groups about 3) for 30 minutes. A 25% solution (V) of the product has a viscosity of 150 cp.

Example 5

100 g of (I) are reacted by the same process as described in Example 1 with 10 g of a diisocyanate with 36 carbon atoms per molecule from technical grade dimerised oleic acid. After reacting for 4½ hours, a 25% aqueous dispersion (VI) of the product has a viscosity of 3400 cp.

Example 6

100 g of a polyamide with an acid number of 6.1 and a base number of 35 (both expressed as mg KOH. g⁻¹) are melted at 150° in a current of nitrogen, and then 0.5 g of powdered sodium hydroxide are added. 290 g of propylene oxide are added dropwise with reflux cooling and with vigorous stirring to avoid excessive refluxing. After the reaction has gone to completion, the current of nitrogen is stopped and 880 g of ethylene oxide are introduced in the manner as described in Example 1. After about 20 hours 1270 g of a waxy, slightly brown product (VII) are afforded, titration of which gives 2145 g per hydroxyl group.

100 g of (VII) are melted with 1.84 g of a blocked diisocyanate (2,4-tolylene diisocyanate which is blocked with 1,1,1-trimethylolpropane and phenol in a molecular ratio of 3:1:3) at 60°, and the liquid is stirred for 30 minutes. The temperature is then increased to 125°, and the mixture is allowed to react for 30 minutes. A 25% aqueous solution (VIII) of the product thus obtained has a viscosity of 3,200 cp.

Example 7

350 g of high molecular polyamide-6 for extrusion (viscosity number 240 according to DIN-53 727 measured from a 0.5 g/dl solution in 96% sulphuric acid) are dissolved at room temperature in 2362 g of 85% formic acid, and diluted with 2177 g of 45% formic acid. After 48 hours, 250 g of nylon are precipitated. The nylon is filtered and washed with about 20 l of cold water until there is no smell of formic acid.

172 g of the powdery, dried nylon-6 are suspended in 1230 g of decalin and then 2 g of sodium hydroxide are added. The process is continued as described in Example 1 and 1305 g of ethylene oxide are added at 150°, after which the decalin is completely removed by vacuum distillation. 1490 g of a bright, waxy, ethoxylated nylon-6 (IX) are thus obtained. Titration of (IX) gives an equivalent weight of 1145 g per hydroxyl group.

100 g of the product (IX) which has been slightly acidified with sulphuric acid (pH value of the 5% aqueous solution 7.8) are melted at 55°. 7.2 g of 4,4'-diphenyl-methane diisocyanate are added dropwise to the melt over the course of 30 minutes, and the mixture is reacted for 30 minutes with constant stirring. The mixture is then heated to 115° and stirred for a further 1½ hours. A 25% aqueous solution (X) of the product thus obtained has a viscosity of 6,500 cp.

Example 8

60.5 g of tris(hydroxymethyl)aminomethane and 15 g of water heated to 95° under a current of nitrogen in a three-necked flask. As soon as a clear solution has formed, 11 g of ethylene oxide are introduced, resulting in an addition reaction. The mixture is then heated to 140° *in vacuo* so that the water is completely distilled off. 1 g of powdered sodium hydroxide is then added, the mixture is stirred, the reaction vessel is rinsed with nitrogen and a further 319 g of ethylene oxide are introduced after which the temperature is maintained at 140-150°. After about 12 hours, the reaction has gone to completion. The reaction vessel is rinsed again with nitrogen and then cooled. 393.5 g of a slightly yellow liquid (XI) are produced, which upon analysis shows an equivalent weight of 200 g per hydroxyl group.

(17)

50 g of (XI) are neutralised with sulphuric acid, so that a 5% aqueous solution has a pH value of 7.00, and then mixed with 11.67 g of hexamethylene diisocyanate at room temperature, and stirred. The reaction mixture is heated to 100°, and after 50 minutes at this temperature, the viscosity begins to increase. The condensation product (XII) is then cooled. (XII) is a highly viscous liquid which is soluble in water, and which features less than 1% of free isocyanate groups.

Example 9

50 g of (XI) (its 5% aqueous solution having a pH of 6.2) are neutralised in a similar manner to that described in Example 8, and the solution is then mixed with 7.25 g of toluylene diisocyanate (80% 2,4- and 20% 2,6-isomer) at 30°. The mixture is then heated to 110° and after 2 hours a highly viscous liquid (XIII) is produced, which readily dissolves in warm water.

Example 10

50 g of (XI) (pH of a 5% solution 7.6) are reacted in a similar manner to that described in Example 8 with 11.6 g of polymethylene polyphenylene isocyanate (isocyanate equivalent weight 139 g, functionality about 3.2) at 90° for 6 hours. 61 g of a brown condensation product (XIV) are produced, the product solidifying at 32° and being readily soluble in water.

Example 11

0.5 g of powdered sodium hydroxide are added to 100 g of anhydrous glycerine, and the mixture is heated to 140-150° under a nitrogen atmosphere. As soon as this temperature has been reached, the nitrogen current is stopped and 334 g of ethylene oxide are gradually added at a speed at which it completely reacts. After about 11 hours, the reaction is complete, and the reaction vessel is rinsed again with nitrogen. 434 g of a slightly cream-coloured liquid (XV) are produced, the analysis of which gives 139 g per hydroxyl group. 50 g of (XV) are neutralised with sulphuric acid (pH of a 5% solution 7.0), and then 16.67 g of polymethylene polyphenylisocyanate (see Example 4) are added at room temperature and the mixture is stirred. The mixture is concentrated at 90°. After 15 minutes, a waxy, slightly brown product (XVI) is produced, which has less than 1% free isocyanate groups.

Example 12

100 g of (XV) are reacted with a further 253 g of ethylene oxide by the method described in Example 11. 353 g of a slightly brown liquid (XVII) are obtained, the analysis of which gives 451 g per hydroxyl group. 50 g of the compound (XVII) are reacted for 10 hours at 110° with 3.22 g of toluylene diisocyanate by the method described in Example 4. A liquid condensation product (XVIII) is obtained which contains less than 0.5% free isocyanate groups.

Example 13

0.5 g of powdered sodium hydroxide are added to 63 g of tetraethylene pentamine under a nitrogen atmosphere, and heated to 125°. As soon as this temperature has been reached, the nitrogen current is stopped and 135.5 g of propylene oxide are added dropwise. After about 20 hours, the propylene oxide has completely reacted, and after heating to 140-150°, 366.7 g of ethylene oxide are introduced under the same conditions as in Example 11. The reaction is complete after 12 hours, and 565 g of a brown, viscous liquid (XIX) are afforded with a hydroxyl equivalent of 1137 g.

100 g of the compound (XIX) are reacted for 10 hours at 115° with 2 g of diphenylmethane-4,4'-diisocyanate, under the same conditions as in Example 5. The resultant thick, liquid condensation product (XX) has less than 0.01% free isocyanate groups.

Example 14

149 g of anhydrous triethanolamine are reacted with 1540 g of ethylene oxide as in Example 11. 1689 g of a slightly brown liquid (XXI) are thus obtained, the analysis of which gives 551 g per hydroxyl group. 100 g of the compound (XXI) are reacted for 4 hours at 115° with 10.3 g of toluylene diisocyanate (mixture of 80% 2,4- and 20% 2,6-isomer) by the method described in Example 5. The resultant, thick, liquid condensation product (XXII) has less than 0.02% free isocyanate groups.

Example 15

384 g of a N-mixed alkyl-propylene diamine, whose alkyl groups consist of a mixture of

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1.3% myristyl, 4.7% palmityl, 42% stearyl, 12% arachidyl and 40% behenyl radicals and with an average molecular weight of 384, are reacted with 2200 g of ethylene oxide by the method described in Example 11. 2584 g of a waxy, yellow product (XXIII) are produced, the analysis of which gives 858.2 g per hydroxyl group. 100 g of the product (XXIII) are reacted for 5 hours at 110° with 6.7 g of tolylene diisocyanate (80% 2,4- and 20% 2,6-isomer) by the method described in Example 5. The resultant waxy condensation product (XXIV) solidifies at 45° and is readily soluble in water.

The ratio of the number of hydroxy groups of the oxalkylated compounds to the number of isocyanate groups in the polyisocyanates in the previous Examples is as follows:

- Example 1 = 2.95
- Example 2 = 4.24
- Example 3 = 2.98
- Example 4 = 9.68
- Example 5 = 7.31
- Example 6 = 3.0
- Example 7 = 1.51
- Example 8 = 1.8
- Example 9 = 3.0
- Example 10 = 3.0
- Example 11 = 3.0
- Example 12 = 3.0
- Example 13 = 7.0
- Example 14 = 1.5
- Example 15 = 1.5

In a similar manner to that described in Examples 8 to 15, the following condensation products may be obtained, which are characterised by the starting materials and the ratio of hydroxy groups : isocyanate groups. The hydroxyalkyl compounds are oxyethylation products and are characterised by the polyfunctional starting material and the number of ethylene oxide units per molecule.

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Example No.	Polyfunctional compound	Number of ethylene oxide units per molecule of polyfunctional compound	OH : NCO ratio
16	triethanolamine	7	polyisocyanate
17	triethanolamine	7	tolylene diisocyanate
18	triethanolamine	15	as Example 6
19	triethanolamine	25	tolylene diisocyanate
20	triethanolamine	35	tolylene diisocyanate
21	triethanolamine	75	tolylene diisocyanate
22	glycerine	30	tolylene diisocyanate
23	trishydroxymethylaminomethane	15	hexamethylene diisocyanate
24	diethylenetriamine	25	tolylene diisocyanate
25	polyamide 11	6 (per amide group)	hexamethylene diisocyanate

Application Example A

20 kg of an unfixed polyester circular net fabric (Simtex 167.30/l) is prewashed for 20 minutes in an aqueous bath at 70°C containing:

1 g/l sodium lauryl sulphonate

1 g/l calcinated soda

and 0.25 g/l product XXII (Example 14) at a goods : liquor ratio of 1:20 in a jet dyeing machine (Then-Flow, registered Trade Mark).

The material is then well rinsed and submitted to a dyeing treatment in the same jet dyeing machine, this time containing a fresh aqueous bath containing :

1 g/l of an anionic dispersing agent (sodium salt of naphthalene-sulphonic acid /CH₂O)

1 % by weight ammonium sulphate

0.4 % by weight C.I. Disperse Red 11

and 0.25 g/l product XXII (Example 14), whose pH is adjusted to 5 by addition of formic acid, at a goods : liquor ratio of 1:20. The temperature of the bath, initially 40°C, is raised to 130°C within 35-40 minutes. Dyeing is continued at 130° for 1 hour, after which the bath is cooled to 70°C and cold rinsed. The dyed polyester material is then removed from the dyeing machine, dried by infra-red irradiation and fixed at 165°C.

It is observed that the dyed polyester material shows practically no signs of creasing.

If the process is repeated without the product XXII in the prewashing and dyeing stages, the material clearly shows visible crease marking.

Application Example B

A nylon spun fabric material of size 2 × 0.3m² is immersed in 10 l of an aqueous dyebath at 40°C containing

2% by weight acetic acid

4% by weight of an anionic levelling agent

and 0.25 g/l product XXII (Example 14) in a winch-beck machine of 50 l capacity and treated therein for 10 minutes. 1.9% by weight of C.I. Acid Blue 40 is then added, and the bath is heated to boiling point. Dyeing is continued for 1 hour at boiling point, and the bath is then warm and cold rinsed. The material is removed from the bath and allowed to dry in air.

It is observed that the dyed material shows practically no signs of creasing.

If the process is repeated without the product XXII, the material clearly shows visible creasing and edge marking.

After the material treated with the product XXII has been dried in a Stenter frame, it is seen to be free of creases, whereas when the untreated material is submitted to the same drying process, crease marks are clearly visible.

Application Example C

The procedure described in Application Example B is repeated, using a bath of the following composition :

1 g/l of an anionic dispersing agent

2 g/l ammonium sulphate

and 0.25 g/l product XXII (Example 14) whose pH is adjusted to 5.5 by addition of formic acid, and to which no dyestuff is added. A practically crease-free fabric results. If this process is repeated without product XXII, the fabric, in contrast, shows clearly visible creases.

WHAT WE CLAIM IS:

1. A wet treatment process for synthetic or semi-synthetic textile material comprising treating the textile material with a liquor containing a polyurethane, which polyurethane is a reaction product of a compound or mixture of compounds 1, the or each compound 1 being a derivative of ammonia; a polyamine; urea; a polyamide; an aminoamide; an aminoalcohol; or a polyol containing up to 10 carbon atoms and up to 6 hydroxyl groups per molecule; in which at least three of the active hydrogen atoms of the amino, hydroxyl and/or amido moieties present are replaced by the same or different groups of formula 1a,



1a

in which each Alkylene, independently, is straight or branched chain (C₂₋₄)-alkylene, unsubstituted or substituted by a phenyl group,

and n is an integer 1 to 100, and a compound or mixture of compounds 2, the or each compound 2 being a hydrocarbon polyisocyanate, in a molar ratio of compound 1 : compound 2 of $\Sigma p : \Sigma r$, p being the number of moles of each compound 1 and r being the number of moles of each compound 2 reacted, Σp and Σr being so chosen that $\Sigma(p.q) \div \Sigma(r.m) = 1.5$ to 21 and $\Sigma p \leq \Sigma(r.m)$, q being the number of groups of formula 1a per



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Application Example A

20 kg of an unfixed polyester circular net fabric (Simtex 167.30/1) is prewashed for 20 minutes in an aqueous bath at 70°C containing:

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1 g/l calcinated soda

and 0.25 g/l product XXII (Example 14) at a goods : liquor ratio of 1:20 in a jet dyeing machine (Then-Flow, registered Trade Mark).

The material is then well rinsed and submitted to a dyeing treatment in the same jet dyeing machine, this time containing a fresh aqueous bath containing :

1 g/l of an anionic dispersing agent (sodium salt of naphthalene-sulphonic acid /CH₂O)

1 % by weight ammonium sulphate

0.4 % by weight C.I. Disperse Red 11

and 0.25 g/l product XXII (Example 14), whose pH is adjusted to 5 by addition of formic acid, at a goods : liquor ratio of 1:20. The temperature of the bath, initially 40°C, is raised to 130°C within 35-40 minutes. Dyeing is continued at 130° for 1 hour, after which the bath is cooled to 70°C and cold rinsed. The dyed polyester material is then removed from the dyeing machine, dried by infra-red irradiation and fixed at 165°C.

It is observed that the dyed polyester material shows practically no signs of creasing.

If the process is repeated without the product XXII in the prewashing and dyeing stages, the material clearly shows visible crease marking.

Application Example B

A nylon spun fabric material of size 2 × 0.3m² is immersed in 10 l of an aqueous dyebath at 40°C containing

2% by weight acetic acid

4% by weight of an anionic levelling agent

and 0.25 g/l product XXII (Example 14) in a winch-beck machine of 50 l capacity and treated therein for 10 minutes. 1.9% by weight of C.I. Acid Blue 40 is then added, and the bath is heated to boiling point. Dyeing is continued for 1 hour at boiling point, and the bath is then warm and cold rinsed. The material is removed from the bath and allowed to dry in air.

It is observed that the dyed material shows practically no signs of creasing.

If the process is repeated without the product XXII, the material clearly shows visible creasing and edge marking.

After the material treated with the product XXII has been dried in a Stenter frame, it is seen to be free of creases, whereas when the untreated material is submitted to the same drying process, crease marks are clearly visible.

Application Example C

The procedure described in Application Example B is repeated, using a bath of the following composition :

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2 g/l ammonium sulphate

and 0.25 g/l product XXII (Example 14) whose pH is adjusted to 5.5 by addition of formic acid, and to which no dyestuff is added. A practically crease-free fabric results. If this process is repeated without product XXII, the fabric, in contrast, shows clearly visible creases.

WHAT WE CLAIM IS:

1. A wet treatment process for synthetic or semi-synthetic textile material comprising treating the textile material with a liquor containing a polyurethane, which polyurethane is a reaction product of a compound or mixture of compounds 1, the or each compound 1 being a derivative of ammonia; a polyamine; urea; a polyamide; an aminoamide; an aminoalcohol; or a polyol containing up to 10 carbon atoms and up to 6 hydroxyl groups per molecule; in which at least three of the active hydrogen atoms of the amino, hydroxyl and/or amido moieties present are replaced by the same or different groups of formula 1a,



1a

in which each Alkylene, independently, is straight or branched chain (C₂₋₄)-alkylene, unsubstituted or substituted by a phenyl group,

and n is an integer 1 to 100, and a compound or mixture of compounds 2, the or each compound 2 being a hydrocarbon polyisocyanate, in a molar ratio of compound 1 : compound 2 of $\Sigma p : \Sigma r$, p being the number of moles of each compound 1 and r being the number of moles of each compound 2 reacted, Σp and Σr being so chosen that $\Sigma(p.q) \div \Sigma(r.m) = 1.5$ to 21 and $\Sigma p \leq \Sigma(r.m)$, q being the number of groups of formula 1a per



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molecule of each compound 1 and m being the number of isocyanate groups per molecule of each compound 2, and which polyurethane is water-soluble or -dispersible to a degree of at least 1 g/l at 20°C, and whose 1 g/l aqueous solution or dispersion at 20°C exhibits a viscosity of no more than 100 cp, the ratio of free hydroxyl groups present in groups of formula 1a to urethane groups in the polyurethane reaction product being from 0.5:1 to 20:1.

2. A wet treatment process according to Claim 1, in which the molar ratio of compound(s) 1 : compound(s) 2, $\Sigma p : \Sigma r$, is so chosen that the ratio of free hydroxyl groups present in groups of formula 1a to urethane groups in the polyurethane reaction product is from 0.5:1 to 10:1.

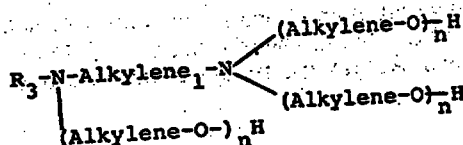
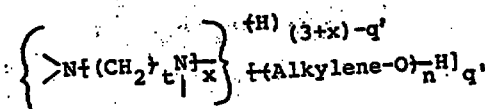
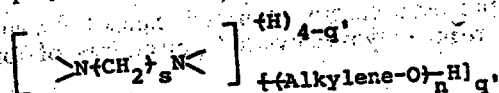
3. A wet treatment process according to Claim 1 or Claim 2, in which the polyurethane reaction product has a water-solubility of at least 10 g/l at 20°C.

4. A wet treatment process according to Claim 3, in which the water-solubility is at least 25 g/l at 20°C.

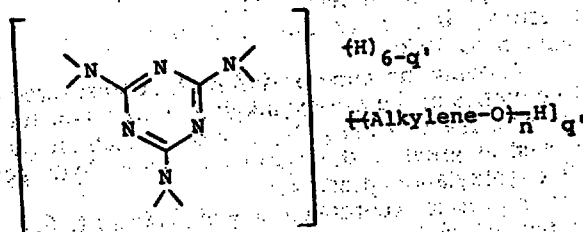
5. A wet treatment process according to any preceding claim, in which the melting point of the polyurethane reaction product does not exceed 150°C.

6. A wet treatment process according to any preceding claim, in which the polyurethane reaction product contains not more than 1% of the unreacted isocyanate groups originally present in the starting compound 2.

7. A wet treatment process according to any preceding claim, in which each compound 1 is selected from the polyoxyalkylated aliphatic polyamines of formulae 11, 12 and 13,



and from polyoxyalkylated melamine of formula 14,



in which s is an integer 2 to 6,

each t, independently, is an integer 2 or 3,

x is an integer 2, 3 or 4,

R₃ is (C₁₋₃₀)alkyl or (C₃₋₂₀)alkenyl,

Alkylene₁ is (CH₂)₂, (CH₂)₃ or (CH₂)₄,

9' is an integer at least 3, its maximum values being 4, (3+x) and 6 for the compounds of formula 11, 12 and 14, respectively,

each Alkylene, independently, is straight or branched chain (C₂₋₄)alkylene, unsubstituted or substituted by a phenyl group,

and n is an integer 1 to 100, the number of alkyleneoxy units present in the or each compound of formula 11, 12 or 14 being at least as great as the number active hydrogen atoms in the amino moieties of the corresponding pre-oxyalkylation precursors thereof.

8. A wet treatment process according to Claim 7, in which each compound 1 is selected from the polyoxyalkylated aliphatic polyamines of formulae 11, 12 and 13.



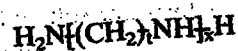
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9. A wet treatment process according to any of claims 1 to 6, in which each compound 1 is selected from polyoxyalkylated polyamides derived from polyamides with an average molecular weight in the range 500-30,000.

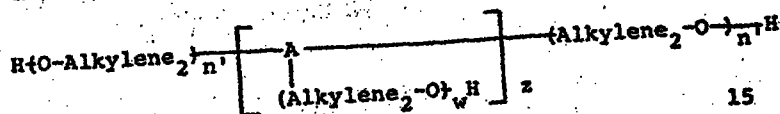
10. A wet treatment process according to any of Claims 1 to 6 and 9, in which each compound 1 is selected from polyoxyalkylated polyamides which are derived from alcohol-soluble nylons with a melting point between 50 and 160°C, which nylons are themselves derived from dimerised (C₁₀₋₂₀)unsaturated fatty acids and di- or polyamines.

11. A wet treatment process according to Claim 10, in which the di- or polyamines are of formula 11a, 12a and 13a

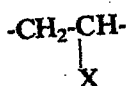


in which s is an integer 2 to 6,
each t, independently, is an integer 2 or 3,
x is an integer 2, 3 or 4,
R₃ is (C₁₋₃₀)alkyl or (C₃₋₂₀)alkenyl,
and Alkylene₁ is -(CH₂)₂, -(CH₂)₃ or -(CH₂)₄.

12. A wet treatment process according to any of Claims 1 to 6 and 9 to 11, in which each compound 1 is selected from polyoxyalkylated polyamides of formula 15,



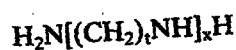
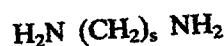
in which A is a repeating unit of an aliphatic, aromatic or araliphatic polyamide, the bond to (Alkylene₂-O)_wH being from the nitrogen atom of a -CON- or -CONH moiety contained in the repeating unit, each Alkylene₂, independently, is a divalent group of formula



wherein X is hydrogen, methyl, ethyl or phenyl,
each n', independently, is an integer 3 to 30,
each w, independently, is 0 or an integer 3 to 30,
and z is an integer 5 to 1000,

each repeating unit A being the same or different, at least three of the active hydrogen atoms of the amido moieties of the pre-oxyalkylation precursor thereof being replaced by the same or different groups (Alkylene₂-O)_nH, and in which the number of (Alkylene₂-O) units present is at least as great as the number of active hydrogen atoms in the amido moieties of the pre-oxyalkylation precursor.

13. A wet treatment process according to any of Claims 1 to 6, in which each compound 1 is selected from polyoxyalkylated amidation products of an aliphatic monocarboxylic acid or a functional derivative thereof and one or more polyamines of formula 11a and 12a,

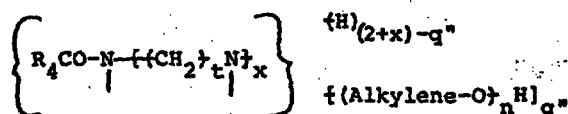
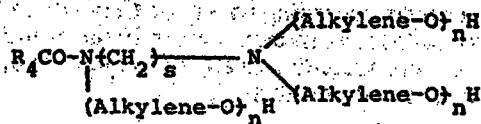


in which s is an integer 2 to 6,
each t, independently, is an integer 2 or 3,
and x is an integer 2, 3 or 4.



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14. A wet treatment process according to Claim 13, in which the polyoxyalkylated amidation products are selected from those of formulae 16 and 17,



in which R_4 is (C_{1-23}) alkyl or (C_{2-19}) alkenyl, s , each t , independently, and x are as defined in Claim 13, each Alkylene, independently, is straight or branched chain (C_{2-4}) alkylene, unsubstituted or substituted by a phenyl group, each n , independently, is an integer 1 to 100, and q'' is an integer at least 3, its maximum value being $(2+x)$, the number of alkyleneoxy units present in a compound of formula 17 being at least as great as the number of active hydrogen atoms in the amino and amido moieties of the corresponding pre-oxyalkylation precursor thereof.

15. A wet treatment process according to any of Claims 1 to 6, in which each compound 1 is selected from polyoxyalkylated derivatives of alkanolamines containing a single amino group and 1 to 3 hydroxyl groups per molecule.

16. A wet treatment process according to Claim 15, in which each compound 1 is selected from polyoxyalkylated derivatives of 2-amino-2-hydroxymethyl-1,3-propane diol, 2-amino-2-methyl-1,3-propane diol, 2-amino-2-ethyl-1,3-propane diol and 2-amino-2-hydroxymethyl-propane.

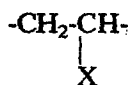
17. A wet treatment process according to any of Claims 1 to 6, in which each compound 1 is selected from polyoxyalkylated derivatives of aliphatic polyols containing 3 to 10 carbon atoms and 3 to 6 hydroxyl groups per molecule.

18. A wet treatment process according to Claim 17, in which the aliphatic polyols are selected from glycerol, 1,1,1-trimethylolpropane, 1,2,4-trihydroxybutane, pentaerythritol, sorbitol, mannitol and tetramethylolcyclohexanol.

19. A wet treatment process according to any of Claims 1 to 6, in which each compound 1 is selected from polyoxyalkylated derivatives of ammonia; of a polyamide; or of a polyamine, urea, an aminoamide, an aminoalcohol or a polyol containing up to 10 carbon atoms and up to 6 hydroxyl groups per molecule, in which 3 to 7 of the active hydrogen atoms are replaced by one or more groups of formula 1a, as defined in Claim 1.

20. A wet treatment process according to Claim 19, in which each compound 1 is selected from polyoxyalkylated derivatives of ammonia; of a polyamide; or of a polyamine, aminoamide, aminoalcohol or polyol containing up to 10 carbon atoms and up to 6 hydroxyl groups per molecule in which 3 to 7 of the active hydrogen atoms are replaced by one or more groups of formula 1a.

21. A wet treatment process according to any of Claims 1 to 11 and 13 to 20, in which Alkylene in the formula 1a or in the group $(\text{Alkylene-O})_2\text{H}$, as the case may be, is a divalent group of formula,



in which X is hydrogen, methyl, ethyl or phenyl.

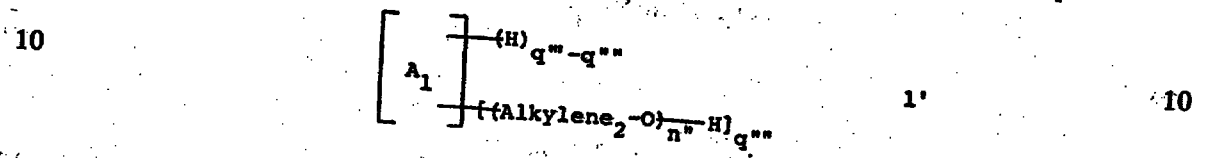
22. A wet treatment process according to any preceding claim, in which Alkylene in the formula 1a or in the group $(\text{Alkylene-O})_n\text{H}$, or Alkylene_2 in the group $(\text{Alkylene}_2\text{-O})_n\text{H}$ or $(\text{Alkylene}_2\text{-O})_w\text{H}$, as the case may be, is a divalent group of formula $-\text{CH}_2-\text{CHX}-$, in which X is hydrogen or methyl.

23. A wet treatment process according to any preceding claim, in which n , n' or w in the group of formula 1a, or in the group $(\text{Alkylene-O})_n\text{H}$, $(\text{Alkylene}_2\text{-O})_n\text{H}$ or $(\text{Alkylene}_2\text{-O})_w\text{H}$

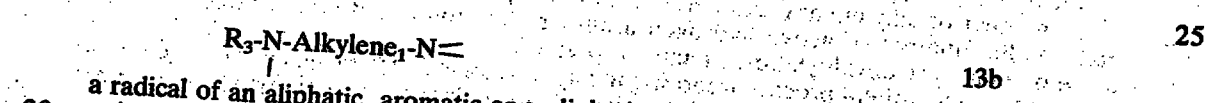
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O₂H, as the case may be, is, except in the case where the compound 1 is a polyoxyalkylated derivative of ammonia, 3 to 50.
 24. A wet treatment process according to Claim 23, in which n, n' is 3 to 30.
 25. A wet treatment process according to any of Claims 1 to 6, and 19 to 22, in which each compound 1 is polyoxyalkylated ammonia and n in the group of formula 1a is 3 to 100.
 26. A wet treatment process according to any of Claims 1 to 6, in which each compound 1 is selected from compounds of formula 1',



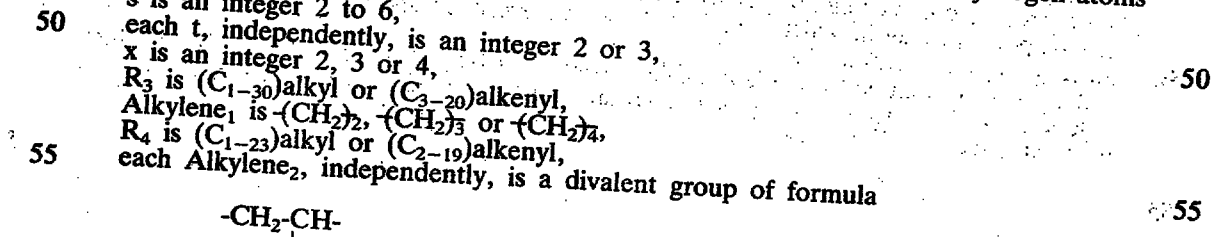
15 in which A₁ is nitrogen,
 a radical 11b, 15



a radical 16b, 30



s is an integer 2 to 6,
 each t, independently, is an integer 2 or 3,
 x is an integer 2, 3 or 4,
 R₃ is (C₁₋₃₀)alkyl or (C₃₋₂₀)alkenyl,
 Alkylene₁ is -(CH₂)₂, -(CH₂)₃ or -(CH₂)₄,
 R₄ is (C₁₋₂₃)alkyl or (C₂₋₁₉)alkenyl,
 each Alkylene₂, independently, is a divalent group of formula 50



60 wherein X is hydrogen, methyl, ethyl or phenyl,
 each n', independently, is, when A₁ is nitrogen, an integer 3 to 100, or, when A₁ is any other of the indicated radicals, an integer 3 to 30,
 q''' is the maximum valency for each radical signified by A₁, being 3 when A₁ is nitrogen, 4 when A₁ is a radical 11b, (3+x) when A₁ is a radical 12b, 3 when A₁ is a radical 13b, 7 to 65



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1002 when A_1 is a radical of a polyamide containing 5 to 1000 repeating units, respectively, 3, 4 or 5 when A_1 is a radical of an alkanolamine containing 1, 2 or 3 hydroxyl groups per molecule, respectively, or 3, 4, 5 or 6 when A_1 is a radical of an aliphatic polyol containing 3, 4, 5 or 6 hydroxyl groups, respectively,

5 and q''' is an integer 3 to q''' , with the provisos that, when A_1 is a polyamide radical, the polymeric chain of the polyoxyalkylated polyamide is terminated at both ends by a group $\{(Alkylene_2-O)_n-H\}_{q'''}$, each repeating unit is the same or different, and the number of $\{(Alkylene_2-O)_n\}$ units present is at least as great as the number of active hydrogen atoms in the amido moieties of the pre-oxyalkylation precursor.

10 27. A wet treatment process according to Claim 26, in which each $Alkylene_2$, independently, is ethylene-1,2- or propylene-1,2.

28. A wet treatment process according to Claim 26 or Claim 27, in which n'' , when A_1 contains 2 or more nitrogen atoms, is 3 to 20.

15 29. A wet treatment process according to any of Claims 26 to 28, in which A_1 is nitrogen or a radical of a polyamide, of an alkanolamine or of an aliphatic polyol.

30. A wet treatment process according to Claim 29, in which A_1 is nitrogen.

31. A wet treatment process according to any preceding claim, in which at least 35 mol % of all the $Alkylene$ or $Alkylene_2$ moieties in the or each compound 1, of formula 15 or of formula 1', as the case may be, are ethylene groups.

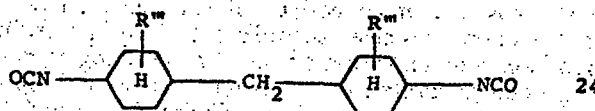
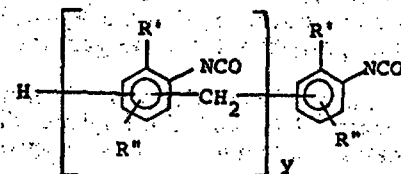
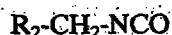
20 32. A wet treatment process according to any preceding claim, in which each compound 2 has 2 to 12 isocyanato substituents per molecule.

33. A wet treatment process according to Claim 32, in which each compound 2 has 2 to 6 isocyanato substituents per molecule.

25 34. A wet treatment process according to Claim 33, in which each compound 2 has 2 to 3 isocyanato substituents per molecule.

35. A wet treatment process according to Claim 34, in which each compound 2 has 2 isocyanato substituents per molecule.

36. A wet treatment process according to Claim 32, in which each compound 2 is selected from those of formula 21, 22, 23 and 24,

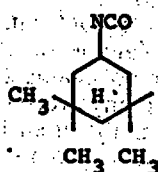
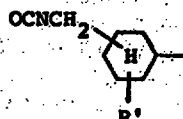
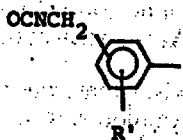


50 in which R_1 is straight or branched chain (C_{2-40}) alkylene; cyclohexylene, saturated or unsaturated with one or two double bonds and unsubstituted or substituted with 1 to 3 (C_{1-2}) alkyl groups; or phenylene, diphenylene or naphthylene, each unsubstituted or substituted with 1 or 2 (C_{1-9}) alkyl groups, the $-NCO$ groups on diphenylene being on different benzene nuclei,

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R_2 is radical of formula,



each R' , independently, is hydrogen or (C_{1-9}) alkyl,
each R'' , independently, is hydrogen or $-NCO$,
each R''' , independently, is hydrogen or methyl,
and y is an integer 1 to 5,

there being no more than 6-NCO groups per molecule in the compounds of formula 23, and any two -NCO groups on the same benzene ring being m- or p- to each other, in the compounds of formula 23.

37. A wet treatment process according to Claim 36, in which each compound 2 is selected from 1,2-dimethyl-diisocyanate, 1,6-hexamethylenediisocyanate and further α,ω -polymethylenediisocyanates containing up to 34 carbon atoms in the polymethylene chain, isophoron diisocyanate, xylylene diisocyanate, 1,3-bis(isocyanatomethyl) cyclohexane, cyclohexylene diisocyanate, 2,4- and 2,6- tolylene diisocyanate, m-phenylene diisocyanate, xylene diisocyanate, 1,5-naphthylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-diphenylene diisocyanate, 3,3'-dimethyl-4,4'-diisocyanato-diphenylmethane and polymethylene polyphenylene isocyanates (compounds of formula 23).

38. A wet treatment process according to Claim 37, in which each compound 2 is selected from hexamethylenediisocyanate, 2,4- and 2,6-tolylene diisocyanates and polymethylene polyphenylene isocyanates containing 2 to 4 isocyanate groups per molecule.

39. A wet treatment process according to any preceding claim, in which the polyurethane reaction product is that obtained by reacting the compound 1 and compound 2 together, in the absence of an added solvent, between 80 and 130°C.

40. A wet treatment process according to any preceding claim, in which the polyurethane reaction product is that obtained by reacting compound 1 with compound 2, the latter having been generated *in situ* from a partially or fully blocked form thereof.

41. A wet treatment process according to Claim 40, in which the blocking of compound 2 has been effected with toluol, unsubstituted phenol, 1,1,1-tris-(hydroxymethyl)ethane and/or 1,1,1-tris(hydroxymethyl) propane.

42. A wet treatment process according to Claim 40 or Claim 41, in which the polyurethane reaction product is that obtained by reacting compound 1 with compound 2 within the temperature range 110-130°C.

43. A wet treatment process according to any preceding claim, in which the process is effected simultaneously with a dyeing, optical brightening, bleaching, washing, boiling or fixation process.

44. A wet treatment process according to Claim 43, in which the process is effected simultaneously with a dyeing process.

45. A wet treatment process according to Claim 44, in which the dye also present in the treatment liquor is an anionic or disperse dyestuff.

46. A wet treatment process according to any preceding claim, in which the synthetic or semi-synthetic textile material treated is selected from cellulose 2½ acetate, cellulose triacetate, polyamide, polyester and polyacrylonitrile.



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47. A wet treatment process according to Claim 46, in which the material is polyamide.

48. A wet treatment process according to any preceding claim, in which the process is conducted at a temperature between 50 and 150°C.

49. A wet treatment process according to any preceding claim, in which the polyurethane reaction product is present in the treatment liquor at a concentration between 0.1 and 5 g per litre.

50. A wet treatment process according to Claim 49, in which the concentration is 0.3 to 1 g per litre.

51. A wet treatment process according to any preceding claim, in which the polyurethane reaction product is added to the treatment liquor before the wet treatment process is begun in the form of an aqueous concentrate containing at least 25% by weight of the polyurethane reaction product.

52. A wet treatment process according to Claim 51, in which the aqueous concentrate contains at least 50% by weight of the polyurethane reaction product.

53. A wet treatment process according to Claim 1, substantially as described herein with reference to any one of the Application Examples A, B and C.

54. A wet treatment process according to Claim 1, in which the polyurethane reaction product is a product substantially as described herein with reference to any one of Examples 1 to 25.

55. A polyurethane reaction product of the reaction between a compound or a mixture of compounds of formula 1', as defined in Claim 26, and a compound or mixture of compounds 2, the or each compound 2 being a hydrocarbon polyisocyanate, in a molar ratio of compound of formula 1' : compound 2 of $\Sigma p' : \Sigma r'$, p' being the number of moles of each compound of formula 1' and r' being the number of moles of each compound 2 reacted, and $\Sigma p'$ and $\Sigma r'$ being so chosen that $\Sigma(p' \cdot q''') \div \Sigma(r' \cdot m) = 1.5$ to 21 and $\Sigma p' \leq \Sigma(r' \cdot m) q'''$ being the number of groups of formula 1'a,



1'a

in which Alkylene₂ and n'' are as defined in Claim 26, per molecule of each compound of formula 1' and m being the number of isocyanate groups per molecule of each compound 2, and which polyurethane product is water-soluble or -dispersible to a degree of at least 1 g/l at 20°C, and whose 1 g/l aqueous solution or dispersion at 20°C exhibits a viscosity of no more than 100 cp, the ratio of free hydroxyl groups present in groups of formula 1'a to urethane groups in the polyurethane product being from 0.5:1 to 20:1, and at least 35 mol % of the Alkylene₂ moieties in the starting material of formula 1' being ethylene groups.

56. A polyurethane reaction product according to Claim 55, in which each Alkylene₂ in the starting material of formula 1' is ethylene-1,2 or propylene-1,2.

57. A polyurethane reaction product according to Claim 55 or Claim 56, in which A_1 in the starting material of formula 1' contains 2 or more nitrogen atoms and n'' therein is an integer 3 to 20.

58. A polyurethane reaction product according to any of Claims 55 to 57, in which A_1 in the starting material of formula 1' is other than a polyamide radical and q''' therein is an integer 3 to 5, when the values 4 or 5 are possible.

59. A polyurethane reaction product according to either of Claims 55 and 56, in which A_1 in the starting material of formula 1' is nitrogen or a radical or a polyamide, of an alkanolamine or of an aliphatic polyol.

60. A polyurethane reaction product according to Claim 59, in which A_1 is nitrogen.

61. A polyurethane reaction product according to Claim 59, in which the starting material of formula 1' is the reaction product of triethanolamine with ethylene oxide.

62. A polyurethane reaction product according to any of Claims 55 to 61 in which the compound 2 starting material is selected from the compounds of formulae 21, 22, 23 and 24, as defined in Claim 36.

63. A polyurethane reaction product according to Claim 62, in which the compound 2 starting material is selected from 1,2-dimethylene-diisocyanate, 1,6-hexamethylenediisocyanate and further α , ω -polymethylenediisocyanates containing up to 34 carbon atoms in the polymethylene chain, isophoron diisocyanate, xylylene diisocyanate, 1,3-bis(isocyanatomethyl) cyclohexane, cyclohexylene diisocyanate, 2,4- and 2,6-tolylene diisocyanate, m-phenylene diisocyanate, xylene diisocyanate, 1,5-naphthylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-diphenylene diisocyanate, 3,3'-dimethyl-4,4'-diisocyanatodiphenylmethane and polymethylene polyphenylene isocyanates (compounds of formula 23).

64. A polyurethane reaction product according to Claim 63, in which each compound 2 starting material is selected from hexamethylenediisocyanate, 2,4- and 2,6-tolylene diisocyanates and polymethylene polyphenylene isocyanates containing 2 to 4 isocyanate

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groups per molecule.

65. A polyurethane reaction product according to any of Claims 55 to 64, in which the polyurethane reaction product is obtained under the reaction conditions defined in any one of Claims 39 to 42.

5 65. A polyurethane reaction product according to Claim 55, substantially as herein described with reference to any one of the Examples 1 to 25.

67. An aqueous concentrate of a polyurethane reaction product as defined in any of Claims 55 to 66 at a concentration of at least 25% by weight.

10 68. An aqueous concentrate according to Claim 67, at a concentration of at least 50% by weight.

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1980.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.