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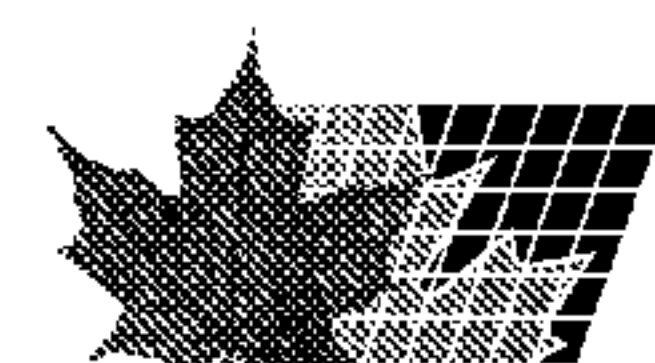
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(54) Titre : DISPERSION AQUEUSE DE POLYSILOXANE ET DE POLYURETHANE, SA PREPARATION ET SON
UTILISATION POUR DES COMPOSITIONS DE REVETEMENT

(54) Title: AQUEOUS POLYSILOXANE-POLYURETHANE DISPERSION, ITS PREPARATION AND USE IN COATING
COMPOSITIONS

(57) **Abrégé/Abstract:**

The invention relates to aqueous dispersions of polysiloxane-polyurethanes based on selected, substantially difunctional starting materials, to their preparation and use for preparing coating compositions, and to a coating composition comprising as substantial binder component polysiloxane-polyurethanes of the kind mentioned. The coating compositions of the invention are especially suitable for use as soft feel coatings.



Abstract:

The invention relates to aqueous dispersions of
5 polysiloxane-polyurethanes based on selected, substantially
difunctional starting materials, to their preparation and
use for preparing coating compositions, and to a coating
composition comprising as substantial binder component
polysiloxane-polyurethanes of the kind mentioned. The
10 coating compositions of the invention are especially
suitable for use as soft feel coatings.

G o l d s c h m i d t AG, Essen

Aqueous polysiloxane-polyurethane dispersion, its
5 preparation and use in coating compositions

The invention relates to aqueous dispersions of polysiloxane-polyurethanes based on selected, substantially difunctional starting materials, to their
10 preparation and use for preparing coating compositions, and to a coating composition comprising as substantial binder component polysiloxane-polyurethanes of the kind mentioned. The coating compositions of the invention are especially suitable for use as soft feel coatings.

15

Modern aqueous binders are capable in many applications of substituting organically dissolved binders. This is so in particular in those segments where aqueous binders may have specific advantages, such as in electrocoating, for
20 example.

For applications having highly specific requirements, such as the painting or coating of plastics with soft feel effect coating materials, there has to date been a
25 lack of satisfactory aqueous binders which meet the requirements imposed.

The level of properties presented by the organically dissolved soft feel coating materials based on

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polyurethane (for example, WO-92/1626 or JP-A-279 620 with the publication number J63132-919-A), particularly in terms of the soft feel effect, the solvent resistance, the mechanical properties of the film and its adhesion to the substrate, is not attained by aqueous systems. In particular, the combination of a good soft feel effect with a satisfactory solvent resistance on the part of the coating is not possible with state of the art aqueous products.

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EP-A-578 940 discloses in this respect water-dispersible polyurethanepolyols based on branched polyesterpolyols.

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The use of aqueous polyester-polyurethane dispersions is described in EP-A-669 352. Here again, the soft feel effect is achieved only by the addition of special flatting agents to the polyester-polyurethane dispersion.

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It is therefore the object of the invention to provide aqueous binders suitable for high-elasticity coating materials, coatings and sealants, especially for soft feel coating materials, which combine a good soft feel effect with good film mechanical properties and adhesion and also a satisfactory solvent resistance and which, furthermore, contain volatile organic substances to the smallest possible extent, so as to be able to meet exacting requirements with respect to environmental compatibility as well.

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It has been possible to achieve this object with the provision of the aqueous polysiloxane-polyurethane dispersions described in more detail below and of the coating compositions based on said dispersions.

5

In a first embodiment the invention provides aqueous dispersions of polysiloxane-polyurethanes having an acid number of from 5 to 100 mg KOH/g polysiloxane-polyurethane solids, a hydroxyl group content of from
10 0.25 to 6.5% by weight, and a urethane group content (calculated as -NH-CO-O-) of from 2.0 to 25.0% by weight, based in each case on polysiloxane-polyurethane solids, wherein the polyurethanes are products, where appropriate at least partly neutralized with bases, of the reaction
15 of

a) a total of from 3 to 25% by weight of at least one linear polydimethylsiloxanediol of the molecular mass range 1,500 to 10,000,

20

b) A total of from 15 to 90% by weight of at least one further difunctional polyol, selected from the group consisting of

25 i) hydroxyl-containing polycarbonates of the molecular mass range 400 to 6,000,

ii) hydroxyl-containing polyetherpolyols of the molecular mass range 350 to 3,500,

5 iii) ester-functional polyesterpolyols obtained from
 dimer fatty acids by hydrogenating the carboxyl
 groups to hydroxyl groups, alkoxyating the
 carboxyl groups or esterifying the carboxyl
 groups with low molecular mass diols, and

 iiii) hydroxyl-containing linear polyesterpolyols of
 the molecular mass range 500 to 4,000,

10

c) a total of from 1 to 10% by weight of at least one
acid component composed of

i) hydroxycarboxylic acids,

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ii) aminocarboxylic acids,

iii) aminosulfonic acids or

20

iv) alkali metal salts of such acids,

25

d) a total of from 0 to 20% by weight of at least one
low molecular mass component composed of at least one
compound containing at least two hydroxyl and/or
amino groups, of the molecular mass range 60 to 300,

e) a total of from 0 to 20% by weight of at least one
hydrophilic monohydric or dihydric alcohol containing

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ethylene oxide units, of the molecular mass range 350 to 3,000,

f) a total of from 5 to 50% by weight of at least one polyisocyanate component composed of at least one organic polyisocyanate of the molecular mass range 168 to 1,000, at least 50% by weight of the polyisocyanate component comprising linear aliphatic diisocyanates of the molecular mass range 166 to 300,

the stated percentages adding up to 100% by weight of the polyurethane fractions of the polysiloxane-polyurethane solids.

The incorporation of relatively high molecular mass polydimethylsiloxanediols with molecular masses above 1,500 g/mol is not possible in accordance with the state of the art, since the severe incompatibility with the organic reaction components only allows an inadequate conversion. Since low molecular mass polydimethylsiloxanes below a molecular mass of 1,500 g/mol do not exhibit soft feel effects, a further object of this invention is to develop a suitable synthesis for polysiloxane-polyurethane dispersions.

This invention accordingly further provides a process for the stepwise preparation of these dispersions, which comprises in a first step preparing an isocyanate-functional prepolymer (I) from components a), b), c), and

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f) and also d) and g) where present in each case, the NCO/OH ratio being from 1.8 : 1 to 3.0 : 1. The resulting prepolymer (I) is then reacted to an isocyanate-functional prepolymer (II) by reaction with component b) and/or d) where present, the NCO/OH ratio being from 1.2 : 1 to 1.6 : 1. Then, by reaction with further polyol as component b) and/or d), this product is converted to the final hydroxyl-containing polysiloxane-polyurethane polymer, in which NCO groups are no longer detectable, and this polymer is dispersed by addition to water in the presence of a neutralizing agent.

The invention also provides for the use of these dispersions for preparing aqueous coating compositions based on water-dispersed binders and crosslinker resins selected from the group consisting of amino resins, optionally hydrophilically modified blocked polyisocyanates, and optionally hydrophilically modified polyisocyanates having free isocyanate groups.

The invention additionally provides aqueous coating compositions, comprising where appropriate the customary auxiliaries and additives, comprising as binder a combination of

A) a polyol component with

B) a crosslinker resin selected from the group consisting of melamine resins, optionally

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hydrophilically modified blocked polyisocyanates, and optionally hydrophilically modified polyisocyanates having free isocyanate groups, wherein from 25 to 100% by weight of the polyol component A) is composed of a hydroxyl-containing polysiloxane-polyurethane of the type present in dispersed form in accordance with the invention and from 0 to 75% by weight of the polyol component A) is composed of binders other than these polysiloxane-polyurethanes.

10

The polysiloxane-polyurethane dispersions of the invention generally have solids contents of from 15 to 68% by weight, preferably from 33 to 60% by weight, and viscosities, determined using a rotational viscometer at 23°C, of from 10 to 20,000 mPas, preferably from 50 to 5,000 mPas. The pH is situated generally between 5 and 10, preferably at from 6 to 8, and is determined in accordance with DIN 53 785 following dilution with distilled water to a solids content of 10% by weight. The term "dispersion" moreover, is intended in the context of the present invention to embrace both true aqueous dispersions and also aqueous solutions. The question of whether a particular system is a dispersion or solution is dependent in particular on the amount of saltlike groups present and on the molecular mass of the polymers.

25

The polysiloxane-polyurethanes present as the disperse phase in the dispersions have in particular, based on solids, a urethane group (-NH-CO-O) content of from 2.0

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to 25.0% by weight, preferably from 4.0 to 19.0% by weight, an acid number of from 5 to 100 mg KOH/g, preferably from 8 to 40 mg KOH/g, the acid number relating both to free acid groups and to base-neutralized acid groups of the solid, and a hydroxyl group content of from 0.3 to 6.5% by weight, preferably from 0.5 to 3.5% by weight. The water dilutability of the polysiloxane-polyurethanes can be attributed essentially to the presence therein of the aforementioned anionic groups.

10

The starting component a) essentially comprises linear, especially α,ω -dihydroxyalkyl, polydimethylsiloxanes of molecular mass 1,500 to 10,000, preferably 2,000 to 4,000, with particular preference 2,000 to 3,000 g/mol.

15

The term "linear" is intended to denote that the compounds contain on average per molecule not more than 0.5, preferably less than 0.3, and with particular preference less than 0.1 branching site, i.e., that the (average) hydroxyl functionality is not more than 2.5, preferably not more than 2.3, and with particular preference not more than 2.1. The term "substantially difunctional" is intended to denote that the compounds contain on average per molecule not more than 0.1 and preferably no branching sites, i.e., that the average hydroxyl functionality is not more than 2.1, and is preferably 2.0.

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The figures given for the molecular mass of the starting components, here and also above and below, are always the average molecular mass which can be calculated from hydroxyl group content and hydroxyl functionality.

5

The polydimethylsiloxanepolyols are preferably linear polydimethylsiloxanes having terminal hydroxyalkyl functions and an average molecular mass of from 1,500 to 3,000, such as Tegomer[®] H-Si 2111 and Tegomer[®] H-Si 2311 (Goldschmidt AG). Likewise suitable are hydroxy(poly-caprolactone)-modified polydimethylsiloxanes, such as Tegomer[®] H-Si 6440 (Goldschmidt AG).

Particular preference is given to the linear hydroxyalkyl-functional polydimethylsiloxane Tegomer[®] H-Si 2311.

Corresponding amino-containing polydimethylsiloxanes such as, for example, Tegomer[®] A-Si 2322 (Goldschmidt AG) can likewise be reacted in accordance with the synthesis of the invention, but produce less weathering-stable coatings.

The corresponding silanol-functional (Si-OH) polydimethylsiloxanes are less preferred on account of the lower reactivity toward isocyanates.

- 10 -

It is likewise possible, of course, but not preferable, to use linear functional polydiphenyl-, polymethylphenyl- or polyalkylsiloxanes as well, or else copolymers thereof.

5

The starting component b) comprises difunctional polyols selected from the group consisting of

- 10 i) hydroxyl-containing polycarbonates of the molecular mass range 400 to 6,000,
- 15 ii) hydroxyl-containing polyetherpolyols of the molecular mass range 350 to 3,500 containing preferably less than 30% by weight of ethylene oxide units, based on all the alkylene oxide units present in the form of polyether chains,
- 20 iii) ester-functional polyesterpolyols obtained from dimer fatty acids by hydrogenating the carboxyl groups to hydroxyl groups, alkoxyating the carboxyl groups or esterifying the carboxyl groups with low molecular mass diols, and
- 25 iv) hydroxyl-containing linear polyesterpolyols of the molecular mass range 500 to 4,000.

The preparation of the polyesterpolyols is described in EP-A-669 352.

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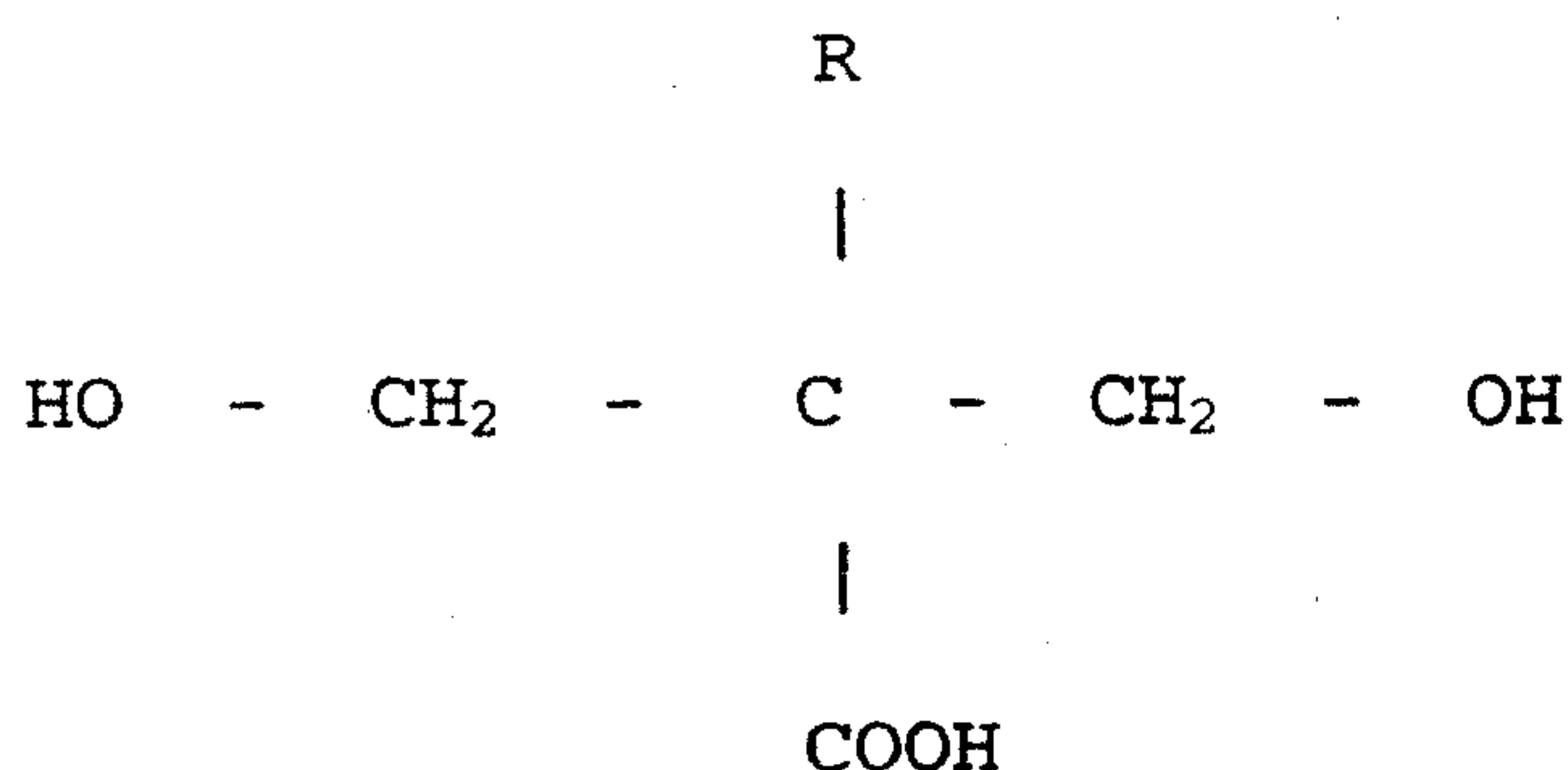
Suitable polycarbonatepolyols are obtained, for example, by reacting carbonic acid derivatives, such as diphenyl carbonate or phosgene, with alcohols, preferably diols. Suitable diols are described, for example, in connection
5 with starting component a2).

Particularly suitable polyetherpolyols are the ethoxylation and/or propoxylation products of water or of diols of the type already exemplified as starting
10 component a2), with the proviso that the ethylene oxide content, based on all the alkylene oxide groups incorporated, is below 30% by weight.

Especially preferred polyols b) are difunctional
15 polyesterdiols of molecular mass 750 to 4,000 and also difunctional polycarbonatepolyols of molecular mass 750 to 4,000.

Starting component c) comprises at least one
20 hydroxycarboxylic acid and/or aminocarboxylic acid and/or aminosulfonic acid and/or hydroxysulfonic acid of the type specified, for example, in US-A-3,479,310. Preferred components c) include 2,2-bis(hydroxymethyl)-alkanemonocarboxylic acids having a total of from 5 to 8
25 carbon atoms, i.e., compounds of the general formula

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in which

R stands for an alkyl radical having 1 to 4 carbon atoms.

Very particular preference as component c) is given to 2,2-dimethylolpropionic acid and 2,2-dimethylolbutyric acid.

As already indicated above, it is also possible, instead of the free acid, to use the corresponding alkali metal salts, provided the salts are sufficiently compatible with the other synthesis components.

Starting component d) comprises compounds containing at least two hydroxyl and/or amino groups, of molecular mass 60 to 300. Suitable examples include ethylene glycol, propylene glycol, neopentyl glycol, butanediol, hexanediol, cyclohexanedimethanol, diethylene glycol, dipropylene glycol, trimethylolpropane, 1,4-cyclohexanediol, glycerol, pentaerythritol, aminoethanol, aminoisopropanol, N,N'-dimethyl-1,3-diaminopropane, and mixtures of these and other corresponding compounds.

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Likewise suitable are low molecular mass reaction products of said compounds with ethylene oxide and/or propylene oxide and/or ϵ -caprolactone.

- 5 Preferred components d) are low molecular mass diols and triols of molecular mass 90 to 150, such as 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, glycerol and/or trimethylolpropane.
- 10 A preferred polyol d) for preparing the prepolymer (I) is a dihydroxy-functional polyol such as 1,4-butanediol; a preferred polyol d) for the further reaction to give the prepolymer (II) is a trifunctional polyol such as trimethylolpropane.

15

- The starting component e) preferably comprises nonionically hydrophilic polyethylene glycols having one or two hydroxyl groups. These are preferably monohydric or dihydric polyether alcohols of the molecular mass
- 20 range 350 to 3,000, as obtained in conventional manner by alkoxyating monohydric or dihydric alcohol starter molecules, using as alkylene oxides ethylene oxide or mixtures of ethylene oxide with up to 40% by weight, based on the total weight of the alkylene oxides, of
- 25 propylene oxide.

One example of starting component e) is Tegomer® D3403 (Goldschmidt AG).

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Starting component f) preferably comprises linear aliphatic diisocyanates of the molecular mass range 168 to 1,000, in particular 168 to 300, such as hexamethylene diisocyanate, undecane 1,11-diisocyanate or dodecane 1,12-diisocyanate. Likewise suitable as starting component f), though less preferred, are mixtures of such linear aliphatic diisocyanates with other diisocyanates such as isophorone diisocyanate or 2,4-diisocyanatotoluene or else with "paint polyisocyanates" based on hexamethylene diisocyanate, of the type known per se having a maximum molecular mass of 1,000. However, at least 50% by weight of starting component f) is composed of linear aliphatic diisocyanates of the type mentioned at the outset.

Examples of suitable solvents for preparing the polysiloxane-polyurethane dispersions include N-methylpyrrolidone, methoxyhexanone, diethylene glycol dimethyl ether, methyl ethyl ketone, methyl isobutyl ketone, acetone, xylene, toluene, butyl acetate, methoxypropyl acetate, and mixtures of these or other solvents. The organic solvents used may be removed from the reaction mixture in whole or in part, where appropriate azeotropically and/or by applying a vacuum or an increased stream of inert gas, before, during or after the dispersing step.

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Suitable catalysts for the urethanization reaction, i.e., the reaction of components a) to f), may be, for example, the following: triethylamine, tin(II) octoate, dibutyltin oxide, dibutyltin dilaurate, and other customary
5 catalysts.

Examples of suitable bases for neutralizing the acid groups incorporated initially include ammonia, N-methylmorpholine, triethylamine, dimethylethanolamine,
10 methyldiethanolamine, morpholine, dimethylisopropanolamine, 2-amino-2-methyl-1-propanol, and mixtures of these and other neutralizing agents. Likewise suitable, though less preferred as neutralizing agents, are sodium hydroxide, lithium hydroxide, and potassium hydroxide.

15

Preferred neutralizing agents are ammonia, triethylamine, dimethylethanolamine, methyldiethanolamine, and dimethylisopropanolamine.

20 The dispersion is prepared, for example, by reacting from 3.0 to 25.0% by weight, preferably from 5.0 to 15.0% by weight, of starting component a) with from 15.0 to 90.0% by weight, preferably from 20.0 to 70.0% by weight, of starting component b), from 1.0 to 10.0% by weight,
25 preferably from 2.0 to 7.0% by weight, of starting component c), from 0 to 20.0% by weight, preferably from 0.5 to 10.0% by weight, of starting component d), and from 0 to 20.0% by weight, preferably from 0 to 10.0% by weight, of starting component e) with from 5.0 to 50.0%

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by weight, preferably from 7.0 to 30.0% by weight, of starting component f), the percentages given for a) to f) adding up to 100% by weight of the polyurethane fractions of the polysiloxane-polyurethane solids, in an organic solution with a concentration of from 40 to 100%, preferably from 85 to 100% (100% = solvent-free), comprising a first step of preparing an isocyanate-functional prepolymer (I) from components a), b), c), and f) and also d) and g) where present, in the presence of a catalyst, wherein the NCO/OH ratio is from 1.8 : 1 to 3.0 : 1, preferably from 2.0 : 1 to 2.5 : 1. The resulting prepolymer (I) is then converted by reaction with component d) where present to give an isocyanate-functional prepolymer (II), wherein the NCO/OH ratio is from 1.2 : 1 to 1.6 : 1.

By reaction with further polyol, where appropriate, as component b) and/or d) the product is subsequently converted to the final hydroxyl-containing polysiloxane-polyurethane polymer, wherein NCO groups are practically no longer detectable.

This convention is generally operated observing an equivalents ratio of isocyanate-reactive groups to isocyanate groups of from 1.2 : 1 to 2.5 : 1, preferably from 1.4 : 1 to 2.0 : 1, so as to end up with reaction products having the aforementioned hydroxyl group content. Any carboxyl groups present in the reaction mixture that are intended for conversion into anionic

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groups are not to be regarded as "isocyanate-reactive" in this context.

Following said conversion, the reaction mixture is dispersed or dissolved in water, with from 25 to 100%, preferably from 45 to 100%, of any acid groups introduced into the reaction mixture having been converted during the reaction or before or during the dispersing step into salt groups by addition of a neutralizing agent. Incorporation of anionic groups in this way is of course unnecessary if salts, especially alkali metal salts, of appropriate amino- and/or hydroxy-carboxylic and/or sulfonic acids have already been employed as synthesis component c).

15

In order to carry out the dispersing step it is possible alternatively to add the water/neutralizing agent mixture to the resin, the resin to the water/neutralizing agent mixture, or the resin/neutralizing agent mixture to the water. By "resin" here is meant either the solventlessly prepared polysiloxane-polyurethane or its solution in one of the auxiliary solvents exemplified. The dispersing step is generally accomplished at a temperature within the range from 20 to 100°C, preferably from 40 to 100°C. The dispersibility of the polysiloxane-polyurethanes in water may be improved if desired by also using external emulsifiers during the dispersing operation.

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The polysiloxane-polyurethane dispersions of the invention generally have an organic solvent content of less than 15% and preferably less than 10% by weight.

5 Following their preparation, it is possible to add further organic solvents to the dispersions of the invention for the purpose of obtaining certain properties, especially alcoholic solvents such as ethanol, n-butanol, n-octanol, butyldiglycol, ethyldiglycol, methyldiglycol or methoxypropanol, for
10 example.

The dispersions of the invention constitute aqueous binder components for coating compositions based on
15 water-dispersed polyhydroxyl compounds and crosslinker resins. In this context the dispersions of the invention may be employed as sole binders or else in a blend with aqueous dispersions of other binders. Accordingly, based on solids, from 25 to 100% by weight of the polyol
20 component of the coating compositions of the invention is composed of polysiloxane-polyurethanes of the type according to the invention and from 0 to 75% by weight is composed of other, water-dispersible or water-soluble binders. Other binders are, in particular, conventional,
25 water-dispersible, optionally hydroxyl-containing polyester resins, polyacrylate resins or polyurethane resins, which differ in their chemical composition from the polysiloxane-polyurethanes of the invention. Preference is given in this context to polyurethane

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resins, as present, for example, in the PU dispersions described in DE-A-26 51 506. These polyurethane resins preferably contain no hydroxyl groups, are of linear construction, and have a molecular weight M_n (numerical average) (calculable from the stoichiometry of the starting materials used to prepare them) of at least 15,000. They are anionically and/or nonionically-hydrophilically modified. Preferred components A) are dispersions containing, based on solids, from 80 to 100% by weight of polysiloxane-polyurethanes of the type according to the invention and from 0 to 20% by weight of the preferred polyurethanes.

Suitable crosslinker resins B) are amino resins, optionally hydrophilically modified polyisocyanates having blocked isocyanate groups, and optionally hydrophilically modified polyisocyanates having free isocyanate groups.

Examples of suitable amino resins are water-dilutable or water-dispersible melamine-formaldehyde and urea-formaldehyde condensation products, as described, for example, in D. H. Solomon, The Chemistry of Organic Filmformers, p. 235 ff, John Wiley & Sons, Inc., New York, 1967. Alternatively, the melamine resins may be replaced in whole or in part by other crosslinking amino resins, as described, for example, in "Methoden der organischen Chemie" (Houben-Weyl), Vol. 14 Part 2, 4th edition, Georg Thieme Verlag, Stuttgart 1963, p. 319 ff.

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Further suitable crosslinker resins include blocked polyisocyanates, based for example on isophorone diisocyanate, hexamethylene diisocyanates, 1,4-
5 diisocyanatocyclohexane, dicyclohexylmethane diisocyanate, 1,3-diisocyanatobenzene, 1,4-diisocyanatobenzene, 2,4-diisocyanato-1-methylbenzene, 1,3-diisocyanato-2-methylbenzene, 1,3-bisisocyanatomethylbenzene, 2,4-bisisocyanatomethyl-1,5-dimethylbenzene, bis(4-iso-
10 cyanatophenyl)propane, tris-(4-isocyanatophenyl)-methane, trimethyl-1,6-diisocyanatohexane or blocked "paint polyisocyanates" such as polyisocyanates containing biuret groups and based on 1,6-diisocyanatohexane, polyisocyanates containing isocyanurate groups and based
15 on 1,6-diisocyanatohexane, or paint polyisocyanates containing urethane groups and based on 2,4- and/or 2,6-diisocyanatotoluene or isophorone diisocyanate on the one hand and low molecular mass polyhydroxyl compounds such as trimethylolpropane, the isomeric propanediols or
20 butanediols or any desired mixtures of such polyhydroxyl compounds on the other, in each case having blocked isocyanate groups.

Likewise suitable are blocked polyisocyanates
25 hydrophilicized, for example, by salt groups of polyether structures.

Examples of suitable blocking agents for these polyisocyanates are monohydric alcohols such as methanol,

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ethanol, butanol, hexanol or benzyl alcohol, oximes such as methyl ethyl ketoxime, lactams such as ϵ -caprolactam, phenols, or CH-acidic compounds such as diethyl malonate, for example.

5

Examples of suitable polyisocyanate crosslinkers B) containing free isocyanate groups include organic polyisocyanates having aliphatically, cycloaliphatically, araliphatically and/or aromatically attached free isocyanate groups, which are liquid at room temperature. Such polyisocyanate crosslinkers B) generally have a viscosity, determined using a rotational viscometer at 23°C, of from 50 to 10,000 mPas, preferably from 50 to 1,500 mPas.

15

Where necessary, the polyisocyanates may be employed as a blend with small amounts of inert solvents in order to lower the viscosity to a level within the specified ranges.

20

Highly suitable, for example, are "paint polyisocyanates" based on hexamethylene diisocyanate or on 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI) and/or dicyclohexylmethane diisocyanate. By "paint polyisocyanates" based on these diisocyanates are meant the derivatives of these diisocyanates that are known per se and contain biuret, urethane, allophanate, uretdione and/or isocyanurate groups and which following their preparation have been freed in a known way, preferably by

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distillation, from excess starting diisocyanate down to a residual content of less than 0.5% by weight. The preferred aliphatic polyisocyanates for use in accordance with the invention include the polyisocyanates which meet
5 the above criteria, contain biuret groups, and are based on hexamethylene diisocyanate, such as may be obtained, for example, by the processes of US Patents 3,124,605, 3,903,126, 3,903,127 and 3,976,622, which are composed of mixtures of N,N',N"-tris-(6-isocyanatohexyl)biuret with
10 minor amounts of its higher homologs, and also the cyclic trimers of hexamethylene diisocyanate which meet the above criteria, as may be obtained in accordance with US-A 4,324,879, composed essentially of N,N',N"-tris-(6-isocyanatohexyl)isocyanurate as a mixture with minor
15 amounts of its higher homologs.

The aromatic polyisocyanates which are likewise suitable in accordance with the invention but less preferred are, in particular, "paint polyisocyanates" based on 2,4-
20 diisocyanatotoluene or its technical-grade mixtures with 2,6-diisocyanatotoluene or based on 4,4'-diisocyanatodiphenylmethane or its mixtures with its isomers and/or higher homologs.

25 Likewise suitable polyisocyanate crosslinkers are those hydrophilicized by the incorporation of polyether groups and/or salt groups, as described, for example, in DE-A-41 36 618 or US-A-4,663,377.

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Preferred crosslinker resins are the above-described polyisocyanate crosslinkers containing free isocyanate groups, especially hydrophilicized crosslinkers on this basis. With particular preference, the polyisocyanate
5 component B) comprises those polyisocyanates or polyisocyanate mixtures containing exclusively aliphatically and/or cycloaliphatically attached isocyanate groups with an (average) NCO functionality of between 2.2 and 5.0 and a viscosity, determined using a
10 rotational viscometer at 23°C, of from 50 to 1,500 mPas.

The coating compositions of the invention generally contain, based in each case on solids, from 50 to 95% by weight, preferably from 65 to 90% by weight, of the
15 hydroxyl-containing component A) in combination with from 4 to 50% by weight, preferably from 5 to 35% by weight, of crosslinker B). The solids content of the coating compositions is generally from 35 to 70% by weight.

20 The coating compositions of the invention may of course include conventional auxiliaries and additives of coatings technology. These include, for example, defoamers, thickeners, leveling assistants, pigments, flatting agents, dispersing assistants for pigment
25 dispersion, and the like.

The coating compositions of the invention which comprise melamine resins or blocked polyisocyanates as crosslinker resins, and coating compositions or sealants based on

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binder combinations of this kind, constitute heat-crosslinkable one-component systems which can be stored at room temperature. Corresponding systems comprising polyisocyanates containing free isocyanate groups as
5 crosslinkers constitute two-component systems, which are obtained by blending the individual components and which have only a limited pot life at room temperature.

The preferred fields of use for the polysiloxane-
10 polyurethane dispersions of the invention include their use as a binder component in elastic coating materials and sealants, especially in soft-feel materials, for the coating of plastics and interior coating of automobiles, for example. However, the polyester-polyurethane
15 dispersions of the invention are also suitable as a binder component for aqueous coating materials for plastics, foils, leather, metal or wood, and also as a binder component for the coating of mineral substrates.

20 Further preferred applications include use as release or antistick coatings and also water vapor permeable and/or dirt-insensitive coatings.

In the formulation of the coatings of the invention, it
25 is of course also possible to combine them with other binders, such as, for example, an anionically and/or nonionically hydrophilically modified, hydroxyl-free PU resin having a molecular mass M_w of at least 15,000.

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Surprisingly it is impossible using the polysiloxane-polyurethane dispersion of the invention to formulate coatings having soft feel properties without the need to use further binders, such as the PU dispersion 1) from EP-B-0 669 352, for example, or solids which influence the tactile properties.

(Unless otherwise specified, the molecular masses are numerical (M_n)).

Examples:

In the examples below all percentages are by weight. The pH values were determined in accordance with DIN 53 785 following dilution with distilled water to a solids content of 10% by weight.

a) Preparation Examples:

Example 1 (inventive):

A reaction vessel with stirring, cooling, and heating means was charged with 84.0 g of the polyester Oxyester T1136 (hydroxyl content about 3.2%, Degussa AG), 24.0 g of the hydroxyalkyl-modified polydimethylsiloxane Tegomer[®]H-Si 2311 (M_w = 2,500 g/mol, Goldschmidt AG), 16.8 g of 2,2-bis(hydroxymethyl)propionic acid (DMPA) and

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54.0 g of N-methylpyrrolidone (NMP) under nitrogen and this initial charge was heated to 60°C and homogenized.

Then 105.7 g of isophorone diisocyanate (IPDI) and 0.2 g of dibutyltin dilaurate (DBTL) were added and the mixture was stirred at 90°C until (about 1 h) the theoretical isocyanate content of about 8% had been reached (prepolymer (I)).

12.0 g of 1,4-butanediol were added to this reaction mixture which was then stirred at 90°C until (about 1 h) the theoretical isocyanate content of about 3.9% had been reached (prepolymer (II)).

Then 27.6 g of trimethylolpropane (TMP) were added and the mixture was stirred at 120 to 130°C until NCO groups were no longer detectable.

After the mixture had been cooled to 100°C, 10.1 g of triethylamine (TEA) and 365.7 g of water were added with stirring.

This gave a polysiloxane-polyurethane dispersion 1) having a solids content of 40%, a hydroxyl group content of 1.8% and an organic solvent content of 7.5%.

Comparative Example 1:

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Preparation was carried out as in Example 1) with the difference that the synthesis took place in accordance with EP-B-0 669 352 (process according to Example 1)) in one step by reacting all the polyol components with the diisocyanate and catalyst until NCO groups were no longer detectable.

This gave an inhomogeneous polysiloxane-polyurethane dispersion 2) in which the polysiloxane Tegomer[®]H-Si 2311 had not been fully incorporated by reaction.

Comparative Example 2:

As a prior art comparative example, the polyester-polyurethane dispersion of Example 1) from EP-B-0 669 352 was chosen.

b) Use Examples:

Use Example 1: (inventive)

50.0 g of the polysiloxane-polyurethane dispersion 1), 3.0 g of silica TS 100 (Degussa AG), 3.0 g of flatting agent Pergopak[®] M3 (Martinswerk, Bergheim), 0.3 g of TEGO[®] Wet KL245 (wetting additive, Tego Chemie Service), 0.5 g of TEGO[®] Foamex 805 (defoamer, Tego Chemie

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Service), 1.0 g of Acrysol RM8 (thickener, Rohm & Haas) and 42.2 g of distilled water were triturated together.

Then 10.0 g of isocyanate crosslinker Desmodur[®] N3300 (Bayer AG) were incorporated by emulsification with stirring.

At 23°C and a relative humidity of about 55%, the paint film was applied to glass or plastic plates, cured at room temperature for 10 minutes and then at 80°C for one hour. The dry film thickness was 50 µm.

The paint properties were tested after the films had been aged (48 hours at room temperature).

15

Use Example 2: (comparative)

Analogous to Use Example 1), the dispersion chosen being that from Comparative Example 1) instead of the polysiloxane-polyurethane dispersion from Example 1).

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Use Example 3: (comparative)

In accordance with the prior art, Use Example 1) from EP-B-0 669 352 was tested.

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The results obtained were as follows:

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The optical properties of the film (film homogeneity, uniformity of the degree of flattening, pigment wetting) of Use Examples 1 and 3 were satisfactory, but the film from Use Example 2 showed severe paint film defects and could not be tested.

Use Example	Dispersion	Soft feel effect ¹	Adhesion ² (cross-cut)	Solvent resistance ³
1) *	1)	1	1	1/1/4/0
2) **	2)	n.d.	n.d.	n.d.
3) **	3)	2	1-2	1/1/4/0

* Inventive

** Comparative

10

1. Value 0 = very good soft feel effect,
Value 2 = good soft feel effect,
Value 5 = no soft feel effect

15

2. Cross-cut according to DIN 53230,
Value 0 = excellent adhesion,
Value 2 = good adhesion,
Value 5 = very poor adhesion

20

3. Exposure carried out for 1 minute with a cotton pad containing solvent,
solvent:

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(premium-grade gasoline/methoxypropyl acetate/xylene/ethanol)

Value 0 = no change,

Value 5 = paint detached,

5 n.d. = not determinable.

Another factor regarded as being of particular advantage of the polysiloxane-polyurethane dispersion of the invention from Example 1) is the fact that even without
10 the use of flatting agents which influence the tactile properties, such as Pergopak[®] M3 or Silitin[®] Z86 (Hoffmann & Söhne KG), for example, it is possible to achieve a pronounced soft feel effect.

15 Use Example 4: (inventive)

50.0 g of the polysiloxane-polyurethane dispersion 1),
3.0 g of silica TS 100 (Degussa AG), 3.0 g of flatting agent Pergopak[®] M3 (Martinswerk, Bergheim), 0.3 g of
20 TEGO[®] Wet KL245 (wetting additive, Tego Chemie Service),
0.5 g of TEGO[®] Foamex 805 (defoamer, Tego Chemie Service), 1.0 g of Acrysol RM8 (thickener, Rohm & Haas) and 42.2 g of distilled water were trituated together.

25 Then 6.0 g of amino crosslinker resin Cymel[®] 327 (American Cyanamid) were added.

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At 23°C and a relative humidity of about 55%, the paint film was applied to glass plates, cured at room temperature for 10 minutes and then at 150°C for 20 minutes. The dry film thickness was 50 µm.

5

The paint properties were tested after the films had been aged (48 hours at room temperature).

Use Example 5: (comparative)

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As the state of the art, a baking formulation formulated with amino crosslinker resin and based on a polyester-polyurethane dispersion in accordance with Use Example 14) from EP-B-0 669 352 was chosen.

15

The results obtained were as follows:

Use Example	Dispersion	Soft feel effect ¹	Adhesion ² (cross- cut)	Solvent resistance ³
4) *	1)	1-2	1	0/0/1/0
5) **	3)	2-3	1-2	0/0/1/0

* Inventive

20 ** Comparative

1. Value 0 = very good soft feel effect,
Value 2 = good soft feel effect,
Value 5 = no soft feel effect

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2. Cross-cut according to DIN 53230,

Value 0 = excellent adhesion,

Value 2 = good adhesion,

5 Value 5 = very poor adhesion

3. Exposure carried out for 1 minute with a cotton pad
containing solvent,

solvent:

10 (premium-grade gasoline/methoxypropyl acetate/xylene/
ethanol)

Value 0 = no change,

Value 5 = paint detached,

n.d. = not determinable.

15

Clearly evident from the comparative examples was the
superiority of the polysiloxane-polyurethane dispersion
of the invention and of the process of the invention for
preparing polysiloxane-polyurethane dispersions.

What is claimed is:

1. An aqueous dispersion of polysiloxane-polyurethanes
5 having an acid number of from 5 to 100 mg KOH/g
polysiloxane-polyurethane solids, a hydroxyl group
content of from 0.25 to 6.5% by weight, and a
urethane group content (calculated as -NH-CO-O-) of
from 2.0 to 25.0% by weight, based in each case on
10 polysiloxane-polyurethane solids, wherein the
polyurethanes are products, where appropriate at
least partly neutralized with bases, of the reaction
of
 - 15 a) a total of from 3 to 25% by weight of at least
one linear polydimethylsiloxanediol of the
molecular mass range 1,500 to 10,000,
 - b) a total of from 15 to 90% by weight of at least
20 one further linear polyol, selected from the
group consisting of
 - i) hydroxyl-containing polycarbonates of the
molecular mass range 400 to 6,000,
 - 25 ii) hydroxyl-containing polyetherpolyols of the
molecular mass range 350 to 3,500,

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iii) ester-functional polyesterpolyols obtained from dimer fatty acids by hydrogenating the carboxyl groups to hydroxyl groups, alkoxyating the carboxyl groups or esterifying the carboxyl groups with low molecular mass diols, and

iiii) hydroxyl-containing linear polyesterpolyols of the molecular mass range 500 to 4,000,

c) a total of from 1 to 10% by weight of at least one acid component composed of

i) hydroxycarboxylic acids,

ii) aminocarboxylic acids,

iii) aminosulfonic acids or

iv) alkali metal salts of such acids,

d) a total from 0 to 20% by weight of at least one low molecular mass component composed of at least one compound containing at least two hydroxyl and/or amino groups, of the molecular mass range 60 to 300,

e) a total of from 0 to 20% by weight of at least one hydrophylic monohydric or polyhydric alcohol

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containing ethylene oxide units, of the molecular mass range 350 to 3,000,

f) a total of from 5 to 50% by weight of at least one polyisocyanate component composed of at least one organic polyisocyanate of the molecular mass range 168 to 1,000, at least 50% by weight of the polyisocyanate component comprising diisocyanates of the molecular mass range 168 to 300,

the stated percentages adding up to 100% by weight of the polyurethane fractions of the polysiloxane-polyurethane solids.

2. An aqueous polysiloxane-polyurethane dispersion as claimed in claim 1, wherein the dispersed polysiloxane-polyurethanes have an acid number of from 8 to 40 mg KOH/g solids, a hydroxyl group content of from 0.5 to 3.5% by weight, and a urethane group content of from 4.0 to 19.0% by weight and constitute products of the reaction of

from 5.0 to 15.0% by weight of component a)
from 20.0 to 70.0% by weight of component b)
from 2.0 to 7.0% by weight of component c)
from 0.5 to 10.0% by weight of component d)
from 0 to 10.0% by weight of component e) and
from 7.0 to 30.0% by weight of component f),
the polydimethylsiloxanediol

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a) being composed of a linear, especially α,ω -dihydroxyalkyl-polydimethylsiloxane of molecular mass in the range from 2,000 to 4,000, component

5 b) being composed of a linear polyesterdiol of molecular mass 500 to 4,000 and/or a linear polycarbonatediol of molecular mass 750 to 4,000, component

10 c) being composed of at least 85% by weight of 2,2-dimethylolpropionic acid and/or 2,2-dimethylolbutyric acid, component

15 d) being composed of at least one low molecular mass diol and/or triol of molecular mass 90 to 150, and component

e) being composed of at least 75% by weight of cycloaliphatic diisocyanates of the molecular mass range 166 to 300,

20 the percentages given for a) to f) adding up in each case to 100% by weight of the polyurethane fractions of the polysiloxane-polyurethane solids.

25 3. A process for preparing an aqueous polysiloxane-polyurethane dispersion as claimed in claim 1 or 2, which comprises in a first step preparing an isocyanate-functional prepolymer (I) from components a), b), c), and f) and also d) and g) where present in each case, the NCO/OH ratio being from 1.8 : 1 to

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3.0 : 1, and then comprises converting the resulting prepolymer (I) into an isocyanate-functional prepolymer (II) by reaction with component d), the NCO/OH ratio being from 1.2 : 1 to 1.6 : 1, and
5 comprises subsequently converting the product by reaction with further polyol as component b) and/or d), to give the final hydroxyl-containing polysiloxane-polyurethane polymer, which is dispersed by addition to water in the presence of a
10 neutralizing agent.

4. The use of an aqueous polyester-polysiloxane dispersion as claimed in claim 1 or 2 for preparing aqueous coating compositions based on water-dispersed
15 binders and crosslinker resins selected from the group consisting of amino resins, optionally hydrophilically modified blocked polyisocyanates, and optionally hydrophilically modified polyisocyanates having free isocyanate groups.

20 5. An aqueous coating composition, comprising where appropriate customary auxiliaries and additives and comprising as binder a combination of

25 A) a polyol component with

B) a crosslinker resin selected from the group consisting of melamine resins, optionally hydrophilically modified blocked polyisocyanates,

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and optionally hydrophilically modified polyisocyanates having free isocyanate groups, wherein from 25 to 100% by weight of the polyol component A) is composed of a hydroxyl-containing polysiloxane-polyurethane as set forth in claim 1 or 2 in dispersion in water and 0 to 75% by weight of the polyol component A) is composed of binders other than these polysiloxane-polyurethanes.

10

6. The coating composition as claimed in claim 5, wherein from 80 to 100% by weight of the polyol component A) is composed of hydroxyl-containing polysiloxane-polyurethanes as set forth in claim 1 or 2 in dispersion in water and from 0 to 20% by weight is composed of binders other than said polysiloxane-polyurethanes.

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