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(54) Title: POLYMER, COMPOSITION AND USE

(57) Abstract: There is described a process for preparing a Schiff base crosslinkable aqueous dispersion of a polyurethane A (PUD) the process comprising(a) reacting components (1) to (4) as present to form an acidic isocyanate terminated prepolymer that comprises anionic or potentially anionic functional groups thereon; where: (1) component one comprises 10 to 80% by weight of at least one polyisocyanate optionally containing at least one anionic or potentially anionic dispersing group; (2) optional component two comprises up to 15% by weight of at least one isocyanate-reactive polyol containing at least one anionic or potentially anionic dispersing group; (3) component three comprises 15 to 85% by weight of at least one isocyanate reactive polyol other than component two if present, and having a weight average molecular weight greater than or equal to 500 Daltons optionally containing at least one anionic or potentially anionic dispersing group; and (4) optional component four comprises up to 20% by weight of at least one isocyanate reactive polyol other than component three and two if present and having a weight average molecular weight less than 500 Daltons; where if component two is not present component one or three contains at least one anionic or potentially anionic dispersing group; where the amounts of components one to four are expressed as a weight percentage calculated from the total amount of the above components (i.e. one and three and optional two and/or four where present) being 100%; and where the mixture used in step (a) is substantially free of volatile amines and N-alkyl pyrrolidinones; (b) adding to the reaction mixture from step (a) an alkali metal neutralising agent in an amount from 0.05 to 6 parts by weight substantially to neutralise the isocyanate terminated prepolymer obtained from step (a); where the amount (in weight parts) of the alkali metal neutralising agent is calculated based on the weight of alkali metal in the neutralising agent relative to the total amount of components one to four in step (a) being equal to 100 parts; and (c) reacting the neutralised prepolymer from step (b) with an active hydrogen compound to extend the chain of the prepolymer to form an aqueous dispersion of polyurethane A. and (ii) 90 to 5% by weight of a vinyl polymer B wherein the weight % amounts of (i) and (ii) are calculated as a percentage of the total amount of (i) and (ii) and these percentages add up to 100%; and where the composition is: substantially free of volatile amines and N-alkyl pyrrolidinones (preferably solvent free); and is neutralised with a metal neutralising agent and the composition comprises a polyamine of polyhydrazide compound. Another aspect of the invention provides an aqueous coating obtained from the above process, in which polyurethane A and/or vinyl polymer B is Schiff base crosslinkable under ambient conditions.

POLYMER, COMPOSITION AND USE

The present invention relates to the field of polyurethanes especially urethane-acrylic based dispersions.

Urethane-acrylic (U-A) dispersions have good resistance to water, chemicals, solvents and abrasion and so are commonly used in coating compositions such as decorative and protective coatings.

To prepare stable aqueous urethane-acrylic dispersions, both the acrylic part and the polyurethane (PU) part must be dispersed in water. This can be achieved in part by surfactants and in part by incorporating suitable groups such as ionic or non-ionic hydrophilic groups in the polyurethane polymer either pendant to the polymer chain or in-chain. Such groups include anions such as carboxylic, sulfonic, sulfate or phosphate groups that are typically incorporated into the PU by reacting compounds containing reactive hydrogen and at least one suitable acid group (typically a carboxylic acid) with polyisocyanate to form the polyurethane component of the urethane-acrylic dispersion. It is undesirable that large amounts of acidic materials remain in the resultant dispersion thus a substantial part (if not all) of the acid present must be neutralised in the final product.

It is also desirable to reduce or eliminate the use of surfactants in an aqueous coating dispersions as the use of large amount of surfactant increases the water sensitivity of the coatings that are formed.

When simple inorganic bases (such as KOH) are added to neutralise anionic polyurethane dispersions to neutralise acid groups therein, they are found unsatisfactory. In general the viscosity of the polyurethane dispersion rises undesirably when strong inorganic bases are added. To prevent the dispersion destabilising the polyurethane, it may be modified with large amounts of hydrophilic groups such as polyethoxy groups. The resultant films and coatings (whether the PU is modified or not) are also highly water sensitive (compared to PUD neutralised by other agents) unless a further agent is added to cross-link the polyurethane. So other neutralising agents are used to prepare commercially available PU dispersions, the most common of which are volatile amines such as the tertiary amine triethyl amine (TEA). These materials are readily available and evaporated from the final film.

However it is known that volatile amines also have various disadvantages. For example they readily evaporate volatile organic compounds (VOC) during the film formation causing unacceptable environmental pollution and/or poor indoor air quality when used indoors. The use of such materials may be more strictly regulated in the future. Therefore it is desirable to find an alternative method of providing stable aqueous urethane-acrylic dispersions and/or neutralising acidic materials used during their preparation.

Various alternatives have been proposed to improve the stability of aqueous urethane dispersions.

US 2968575 describes a PU latex dispersed in water using an emulsifier.

US 4,501,852 describes stable aqueous dispersions of polyurethane-ureas containing (i) 10-120 meq per 100 g of anionic groups chemically incorporated therein and (ii) up to about 10% by weight of hydrophilic chains containing ethylene oxide (EO) units. To counter the anionic groups the formulation contains a mixture of volatile and non-volatile cations in an equivalent ratio from about 1:4 to 4:1. The examples use as component (ii) a non-ionic polyether monoalcohol of n-butanol, ethylene oxide and propylene oxide (in a molar ratio 83:17) having an OH-number of 26. This component aids dispersion but increases water sensitivity. The examples also use the undesirable NMP as a solvent.

US 4,701,480 describes aqueous polyurethane-urea dispersions with improved hydrolytic stability formed from an aqueous polyurethane-urea-dispersion containing carboxylic acid groups neutralized with volatile organic bases which are then converted to non-volatile cations by adding alkali metal salts of organic or inorganic acids in an amount sufficient to displace at least a portion of the volatile organic bases. The volatile organic bases may be optionally removed by distillation under reduced pressure. All the examples contain NMP and distillation is undesirable because it uses large amounts of energy and may cause excessive foaming (as described in US 2010/0099967 in comparative example XVI).

US 2006-0229409 describes polyurethane dispersions made from TMXDI with a special embodiment on page 9 where the use of metal hydroxides is mentioned. This is not exemplified in the examples nor is TMXDI a suitable diisocyanate for use in coatings (it is too soft).

US 2010-0098867 (Costa) describes a method of making aqueous dispersions of carboxylated anionic polyurethanes that are free of volatile amines and do not contain any polyoxyethylene or polyoxypropylene side chains. First a prepolymer (containing 2-10% by weight of isocyanate groups and 10-100 meq of carboxylic groups) is prepared by reacting: a polyol with a carboxylic acid group; a non-ionic polyol, and a (cyclo)aliphatic polyisocyanate. The prepolymer is dispersed in an aqueous solution of an alkaline metal hydroxide and then the prepolymer is chain extended with a polyamine.

EP1153051 describes aqueous dispersions of anionic polyurethanes with pendant carboxylic acid groups that are neutralised with a reactive volatile amine compound (tertiary amino functional acrylic monomer (DMAEMA)) that is subsequently incorporated in the polymer backbone by radical polymerization. Unreacted free monomer remains in the final product which thus still contains volatile amines. The monomer may also contain impurities in the monomer and hydrolysis may generate the undesirable side product dimethylethanol amine.

WO93/24551 describes an aqueous polyurethane polymer dispersion comprising the reaction product of: organic polyisocyanate; polyester polyol which incorporate polymerized units derived from dimer acid; non-ionic and/or ionic dispersing groups and at least one of the following polymerized units: cyclo-aliphatic polyol of molecular weight (Mw) < 400; cyclo-aliphatic polyacid of MW < 400, aromatic polyol MW< 500, aromatic diacid Mw < 500 and an active hydrogen chain extending compound.

WO 2001-027179 (Stahl) describes an anionic polyurethane dispersion which is neutralised by a tertiary amine functional urethane polymer or oligomer. Although the polymeric material is less volatile than reagents such as TEA, this method adds extra expense and complexity to preparation of the PU dispersion and is not completely successful at removing all acidic groups.

Surprising the applicant has found a means to stabilise aqueous dispersions of acrylate and anionic polyurethanes without the proceeding disadvantages.

In particular the applicant has found that adding an alkali metal neutralising agent at an early stage in the process reduces or avoids some or all of the preceding problems with the prior art.

Therefore broadly the invention comprises a process for preparing an aqueous dispersion of a polyurethane [A], the process comprising the steps of:

(a) reacting components one and three (and two and four where present) to form an acidic isocyanate terminated prepolymer that comprises anionic or potentially anionic functional groups thereon; where:

(1) component one comprises 10 to 80% by weight of at least one polyisocyanate optionally containing at least one anionic or potentially anionic dispersing group;

(2) optional component two comprises up to 15% by weight of at least one isocyanate-reactive polyol containing at least one anionic or potentially anionic dispersing group;

(3) component three comprises 15 to 85% by weight of at least one isocyanate reactive polyol other than component two if present, and having a weight average molecular weight greater than or equal to 500 Daltons, optionally containing at least one anionic or potentially anionic dispersing group; and

(4) optional component four comprises up to 20% by weight of at least one isocyanate reactive polyol other than component three and two if present and having a weight average molecular weight less than 500 Daltons;

where if component two is not present component one or three contains at least one anionic or potentially anionic dispersing group;

where the amounts of components one to four are expressed as a weight percentage calculated from the total amount of the above components (i.e. one and three and optional two and/or four where present) being 100%; and

where the mixture used in step (a) is substantially free of volatile amines and N-alkyl pyrrolidinones;

(b) adding to the reaction mixture from step (a) an alkali metal neutralising agent in an amount from 0.05 to 6 parts by weight substantially to neutralise the isocyanate terminated prepolymer obtained from step (a);

where the amount (in weight parts) of the alkali metal neutralising agent is calculated based on the weight of alkali metal in the neutralising agent relative to the total amount of components one to four in step (a) being equal to 100 parts; and

(c) reacting the neutralised prepolymer from step (b) with an active hydrogen compound to extend the chain of the prepolymer to form an aqueous dispersion of polyurethane A.

It will be seen that the sum of the amounts of ingredients given (a) and (b) together will total greater than 100 parts by weight.

In the process of the invention any of components (1) (2) and/or (3) (i.e. any of these by themselves or any combination) may comprise at least one anionic or potentially anionic dispersing group. However it is preferred that the isocyanate component (1) does not contain an anionic or potentially anionic dispersing group but instead at least one such group comprises the polyol component (2).

Therefore in one embodiment of the process of the invention, step (a) comprises:

(a) reacting:
  (1) 10 to 80% by weight of at least one polyisocyanate;
  (2) 1 to 15% by weight of at least one isocyanate-reactive polyol containing at least one anionic or potentially anionic dispersing group;
  (3) 15 to 85% by weight of at least one isocyanate reactive polyol other than (2), and having a weight average molecular weight $\geq$ 500 Daltons optionally comprising at least one anionic or potentially anionic dispersing group; and
  (4) optionally up to 20% by weight of at least one isocyanate reactive polyol other than (2) and (3) and having a weight average molecular weight < 500 Dalton; to form an acidic isocyanate terminated prepolymer that comprises anionic or potentially anionic functional groups and which is substantially free of volatile amines and N-alkyl pyrrolidinones (such as TEA, NMP or NEP).

Preferably step (b) occurs during or substantially immediately after step (a).

Without being bound by any mechanism it is believed that in step (b) the metal cation from the alkali metal neutralising agent forms a counterion for the anionic group thereon (and/or anionic group formed from the potential anionic groups thereon)

A further aspect of the invention provides a process for preparing an aqueous coating composition comprising bringing into intimate admixture components (i) and (ii):

(i) 10% to 95%, preferably 20% to 80%, more preferably 30% to 65% by weight of a polyurethane dispersion A obtained and/or obtainable by the process of the invention as described herein; and
(ii) 90% to 5%, preferably 80% to 20%, more preferably 70% to 35% by weight of a vinyl polymer B optionally having a glass transition temperature $\geq$ 15°C

wherein

(i) and (ii) add up to 100% and are calculated based on weight of solids (excluding the water); and where the composition (and both components (i) and (ii)) are substantially free of volatile amines and N-alkyl pyrrolidinones.

Preferably both components (i) and (ii) form different phases which are present in the same particles.

Preferably in the process of the invention as described above the polyurethane A and/or the vinyl polymer B are self cross-linkable, preferably Schiff base cross-linkable, under ambient conditions. More preferably the polyurethane A comprises a carbonyl group capable of undergoing Schiff base self-cross-linking.

A still further aspect of the invention provides an aqueous coating composition obtained and/or obtainable by a process of the invention.

Use of Schiff base crosslinkers has been described to make polyurethane foams. For example US4016113 describes use of certain aromatic or Spiro diamine Schiff bases to cross-link PU foams. Schiff base crosslinking of PU foams has also been described in US3321433, US3657192, US3890255, US3907721 and US3926867

However polyurethane foams are different from aqueous PU dispersions and especially from urethane acrylate dispersions where Schiff base crosslinking has not been used to improve stability. Surprisingly a Schiff base crosslinking reaction still occurs at alkaline environment. This was because urethane acrylic dispersions are typically alkaline but become acidic on drying (as amine evaporates) and it was believed that a low pH (acidic conditions) were essential for self crosslinking. In a system such as those of the present invention described herein (which are permanently alkaline) Schiff base cross-linking would not be expected to work.

For example see Journal of Applied Polymer Science Vol104 p3948 2007: ‘Acid condition is indispensable for the crosslinking reaction between diacetone acrylamide and adipic acid dihydrazide. Acrylic acid is usually incorporated into copolymer to give an acid condition to facilitate the crosslinking reaction.’ (page 3948, column 2 lines 26 to 33)

Also Journal Coat Technol. Res 5(3) p285 (2008) in the section discussing the ‘’Fundamentals of keto-hydrazide crosslinking” states: ‘Comparison of the initial rates of the reactions under different pH conditions clearly shows that the chemical reaction rate increases with decreasing pH, as illustrated in Fig. 4. We conclude then that the reaction is acid catalysed.’ (page 288, column 2, lines 27 to 31). The section headed “Conclusions” states: ’Moreover, the crosslinking reaction is acid catalysed and the reaction rate increases as pH decreases.' (page 296, column 1, lines 21 to 23)

It can be seen that there is a technical prejudice against using Schiff base cross-linked acrylic polymers in non-acidic (neutralised) or alkaline systems. As it is well known that PU dispersions are acidic must be neutralised (for the reasons stated herein), Schiff base crosslinking has not been used in permanent alkaline systems.

The applicant has found surprisingly that the urethane acrylic systems when permanently alkaline neutralized can still be self cross-linked via a Schiff base mechanism. In particular the applicant has found that these acidic aqueous PU dispersions that are subsequently neutralised may contain Schiff base crosslinkable urethane and/or vinyl polymers to produce urethane acrylic dispersions that reduce or avoid some or all of the preceding problems with the prior art.

Therefore broadly the present invention provides an aqueous coating composition comprising:

(i) 10 to 95% by weight of a Schiff base crosslinkable polyurethane A obtained by the reaction of:

  (a) an isocyanate terminated prepolymer formed from components one to five comprising:

    (1) 10 to 80 parts by weight of at least one polyisocyanate

    (2) 1 to 15 parts by weight of at least one isocyanate-reactive polyol containing at least one anionic or potentially anionic dispersing group

    (3) 15 to 84 parts by weight of at least one isocyanate reactive polyol other than (2) of weight average molecular weight $\geq$ 500 Daltons; optionally containing at least one anionic or potentially anionic dispersing group.

    (4) optionally up to 20 parts by weight of at least one isocyanate reactive polyol other than (2) or (3) of weight average molecular weight < 500 Daltons

    (5) 0.05 to 6 parts by weight of an alkali metal neutralising agent (preferably whose cation acts as counterion of the anionic group of (2)).

where the amounts of (1), (2), (3), (4) and (5) are calculated as a weight parts relative to the total amount of components (1) to (5) being 100 weight parts. Component 3 and/or 4 contain Schiff base crosslinkable carbonyl groups

(b) an active hydrogen chain extending compound; and

(ii) 90 to 5% by weight of a Schiff base cross-linkable carbonyl groups containing vinyl polymer B wherein the weight % amounts of (i) and (ii) are calculated as a percentage of the total amount of (i) and (ii) and these percentages add up to 100%; and

where the composition is:

substantially free of volatile amines and N-alkyl pyrrolidinones (preferably solvent free); and

is neutralised with a metal neutralising agent and the composition comprises a polyamine of polyhydrazide compound.

Alternatively, the present invention provides an aqueous coating composition comprising:

(i) 10 to 95% by weight of a Schiff base crosslinkable polyurethane A obtained by the reaction of:

(a) an isocyanate terminated prepolymer formed from components one to five comprising:

(1) 10 to 80 parts by weight of at least one polyisocyanate

(2) 1 to 15 parts by weight of at least one isocyanate-reactive polyol containing at least one anionic or potentially anionic dispersing group

(3) 15 to 84 parts by weight of at least one isocyanate reactive polyol other than (2) of weight average molecular weight $\geq$ 500 Daltons; optionally containing at least one anionic or potentially anionic dispersing group.

(4) optionally up to 20 parts by weight of at least one isocyanate reactive polyol other than (2) or (3) of weight average molecular weight < 500 Daltons

(5) 0.05 to 6 parts by weight of an alkali metal neutralising agent (preferably whose cation acts as counterion of the anionic group of (2)).

where the amounts of (1), (2), (3), (4) and (5) are calculated as a weight parts relative to the total amount of components (1) to (5) being 100 weight parts. Component 3 and/or 4 contain Schiff base crosslinkable carbonyl groups

(b) an active hydrogen chain extending compound; and

(ii) 90 to 5% by weight of a vinyl polymer B wherein the weight % amounts of (i) and (ii) are calculated as a percentage of the total amount of (i) and (ii) and these percentages add up to 100%; and

where the composition is:

substantially free of volatile amines and N-alkyl pyrrolidinones (preferably solvent free); and

is neutralised with a metal neutralising agent and the composition comprises a polyamine of polyhydrazide compound

Alternatively, the present invention provides an aqueous coating composition comprising:

(i) 10 to 95% by weight of a polyurethane [A] obtained by the reaction of:

(a) an isocyanate terminated prepolymer formed from components one to five comprising:

(1) 10 to 80 parts by weight of at least one polyisocyanate

(2) 1 to 15 parts by weight of at least one isocyanate-reactive polyol containing at least one anionic or potentially anionic dispersing group

(3) 15 to 84 parts by weight of at least one isocyanate reactive polyol other than (2) of weight average molecular weight $\geq$ 500 Daltons; optionally containing at least one anionic or potentially anionic dispersing group.

(4) optionally up to 20 parts by weight of at least one isocyanate reactive polyol other than (2) or (3) of weight average molecular weight < 500 Daltons

(5) 0.05 to 6 parts by weight of an alkali metal neutralising agent (preferably whose cation acts as counterion of the anionic group of (2)).

where the amounts of (1), (2), (3), (4) and (5) are calculated as a weight parts relative to the total amount of components (1) to (5) being 100 weight parts.

(b) an active hydrogen chain extending compound; and

(ii) 90 to 5% by weight of a Schiff base crosslinkable carbonyl groups containing vinyl polymer B wherein the weight % amounts of (i) and (ii) are calculated as a percentage of the total amount of (i) and (ii) and these percentages add up to 100%; and

where the composition is:

substantially free of volatile amines and N-alkyl pyrrolidinones (preferably solvent free); and

is neutralised with a metal neutralising agent and the composition comprises a polyamine of polyhydrazide compound.

Another aspect of the invention provides an aqueous coating as claimed immediately above, in which polyurethane A and/or vinyl polymer B is Schiff base cross-linkable under ambient conditions.

The following components may preferably be present in the following amounts by weight given as parts by weight or percentages by weight of the total amount of components (1) to (5) where present.

Preferably component (1) (the polyisocyanate) is present in an amount from 15 to 70, more preferably from 20 to 60, most preferably 25 to 50 by weight.

Preferably component (2) (the anioinic isocyanate-reactive polyol) is present in an amount from 2 to 12, more preferably from 3 to 10, most preferably 4 to 7 by weight.

Preferably component (3) (the high (>500D) mw isocyanate-reactive polyol) is present in an amount from 20 to 80, more preferably from 25 to 75, most preferably 30 to 60 by weight.

Preferably optional component (4) (the low (<500D) mw isocyanate-reactive polyol) is present in an amount from 0.5 to 20, more preferably from 1 to 15, most preferably 2 to 10 by weight.

Preferably optional component (5) (the alkali metal neutralising agent) is present in an amount from 0.1 to 6, more preferably from 0.2 to 5, most preferably 0.5 to 4 by weight.

The term ''alkali metal neutralising agent'' denotes an alkali metal compound, preferably an alkali metal salt, that is sufficiently basic under the conditions (under which the polyurethane dispersion is prepared) to neutralise the acidic groups on the polymer. Without wishing to be bound by any mechanism it is believed that ions from the alkali metal neutralising agent act as counter ions to ionic groups formed from acidic groups on the polymer. Preferred alkali metal salts comprise cations such as potassium, sodium and/or lithium with sodium being more preferred. Preferred alkali metals salt comprise anions such as carbonate, bicarbonate, hydroxide and/or hydride, with hydroxide being more preferred. The most preferred alkali metal neutralising agents are sodium and/or potassium hydroxide.

The polyurethane dispersions of the invention may (unless indicated otherwise herein) be prepared conventionally using conventional polyols and isocyanates.

For example the polyisocyanate used in the present invention as component one may be selected from those described in WO2007-006586 as polyisocyanate component (i) (see from page 7, line 33 to page 8, line 20 – this passage incorporated herein by reference).

For example the NCO-reactive polyols used in the present invention as components two, three and four (subject to the other requirements for these components specified herein) may be selected from those described in WO2007-006586 as components (ii), (iii) and/or (iv) (see from page 8, line 30 to page 9, line 24 – this passage also incorporated herein by reference)

The term ''ambient self cross-linkable'' denotes a polymer that under ambient conditions will form covalent bonds between different functional groups on different polymer chains to form cross links without the addition of additional separate crosslinker. Preferred self cross-linking urethane-acrylic polymers are those that bear both carbonyl functional groups and carbonyl reactive amine and/or hydrazine functional groups to impart crosslinkability to the urethane-acrylic polymer. Preferably either polyurethane [A] or vinyl polymer [B] are capable of self cross-linking by a Schiff base reaction under ambient conditions (also known as Schiff base cross-linking). Alternatively both polyurethane A and vinyl polymer B are capable of self-crosslinking by Schiff base reaction under ambient conditions.

Without wishing to be bound by any mechanism it is believed that in Schiff base crosslinking the carbonyl and (C=O reactive) amine / hydrazine groups react together in a Schiff base reaction to link the polymer chains. The carbonyl groups may be incorporated into the vinyl polymer by the free-radical addition polymerisation of at least one carbonyl-containing mono-ethylenically unsaturated monomer (e.g. diacetone diacrylamide (DAAM). The carbonyl reactive amine and/or hydrazide groups may be introduced by addition of polyamine and/or polyhydrazide compounds (e.g.

adipic acid dihydrazide) Similarly a carbonyl functional component (3) can be used to incorporate Schiff base reactable groups in the polyurethane.

Component one comprises a polyisocyanate. Suitable polyisocyanates may comprise aliphatic, cycloaliphatic, araliphatic, aromatic and/or polyisocyanates modified by the introduction of urethane, allophanate, urea, biuret, carbodiimide, uretonimine, urethdione or isocyanurate residues. Examples of suitable polyisocyanates include ethylene diisocyanate, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, cyclohexane-1, 4-diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, p-xylylene diisocyanate, α,α'-tetramethylxylene diisocyanate, 1,4-phenylene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, polymethylene polyphenyl polyisocyanates, 2,4'-diphenylmethane diisocyanate, 3(4)-isocyanatomethyl-1-methyl cyclohexyl isocyanate, 1,5-naphthylene diisocyanate and mixtures thereof. Preferred polyisocyanates are isophorone diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, toluenediisocyanate and 4,4'-diphenylmethane diisocyanate.

Components two, three and four comprises various polyols as defined herein. Suitable polyols may comprise propylene glycols, poly(propylene oxide/ethylene oxide) copolymers, polytetrahydrofuran, polybutadiene, hydrogenated polybutadiene, poysiloxane, polyamide polyesters, isocyanate-reactive polyoxyethylene compounds, polyester, polyether, polyether ester, polycaprolactone, polythioether, polycarbonate, polyethercarbonate, polyacetal and polyolefin polyols.

Preferably component two comprises a polyol with an anionic or potential anionic dispersing group thereon.

Preferred anionic dispersing groups are carboxylic, phosphate, phosphonate or sulfonic acid groups. Preferred potentially anionic dispersing groups are precursors for the anionic dispersing groups described herein, i.e. groups which under the conditions of step (a) will transform into the anionic dispersing groups. Most preferred anionic dispersing groups are carboxylic or sulfonic acid groups. Conversion to the salt form is achieved by neutralisation of anionic groups with an alkali metal neutralising agent during step (a).

Component three comprises a isocyanate reactive polyol with a weight average molecular weight of greater than 500 daltons (high mw polyol). Component four comprises a isocyanate reactive polyol with a weight average molecular weight of less than 500 Daltons.

In case of polyurethane A is Schiff base crosslinkable, preferably component 3 contains carbonyl groups suitable for Schiff base crosslinking. The carbonyl content of component 3 is 0.1-10 meq carbonyl/gr polyol, preferably 0.5-5 meq carbonyl/gr polyol, most preferably 1-3 meq carbonyl/gr polyol.

The presence of carbonyl (i.e. aldo or ketone) functional groups in the examples of the present invention can be determined by any suitable known method such as by means of ^{13}C resonances in ^{13}C mnr spectrum. For ketones and aldehyde carbonyl groups these generally appear from 190 to 210 ppm irrespective of the side-chain substituents. These can be distinguished from carbon 13 resonances from other C=O groups such as in carboxylic acid derivatives (amides, esters, carboxylic acids, acid chlorides etc.) which generally appear from 160 to 185 ppm. For example in one suitable method the ^{13}C NMR spectra of a 200 mg sample in 600 microlitres of a carrier medium of $CDCl_3$ and Chromium (III) acetylacetonate (also denoted as $Cr(acac)_3$) may be recorded. Alternatively the presence of carbonyl groups (i.e. aldo or ketone) in the process of the invention can be determined from relevant absorption peaks in the infra-red spectrum of the reaction mixture. From these or other known methods the amount of unreacted carbonyl groups present in sample can be determined.

In case of polyvinyl polymer B is Schiff base crosslinkable, the vinyl polymer contains carbonyl groups suitable for Schiff base crosslinking. Preferably the vinyl polymer contains 0.1-20 wt% of a carbonyl functional monomer on total monomers, more preferably 0.5-10 wt% of a carbonyl functional monomer on total monomers, most preferably 1-5 wt% of a carbonyl functional monomer on total monomers.

Preferably the equivalent ratio of amine groups to carbonyl groups is 0.2 to 1.5, more preferably 0.35 to 1.1, most preferably 0.6 to 0.9.

In one embodiment of the invention it is preferred that the acrylic urethane of the invention and/or prepared according to the process of the invention is substantially free of any non-ionic functional polyols as it is believed that such components may deteriorate water resistance.

In a still further embodiment of the invention it is preferred that the polyurethane dispersions (PUD) and/or the urethane acrylics of or prepared in the present invention are permanently basic (i.e. after neutralisation with the alkali metal neutralising agent), preferably exhibiting a pH of > 8. Although PUDs and urethane acrylic coatings with a high pH were thought to be undesirable, the applicant has surprisingly found that they may solve some or all of the problems identified herein.

Optionally additional surfactant may be added to facilitate dispersing the urethane however this is not preferred as it has a detrimental effect on the water resistance.

In the present invention it is preferred that the neutralising agent is added to the prepolymer as by pre-neutralizing the prepolymer urethanes with lower acid values can be synthesized which have improved water resistance. More preferably the neutralizing agent is added as aqueous solution.

Preferred compositions of the invention have low acid values (AV), more preferably the AV of the total composition is from 1 to 40 mg KOH / g, more preferably 2-20 mg KOH/g, most preferably 3-15 mg KOH/g.

Without wishing to be bound by any mechanism it is believed that (alkali) metal ion neutralized urethane-acrylic based dispersions contain sufficient ambient self crosslinkable groups to compensate for the deteriorated chemical stain resistances, specifically water resistance and optionally may also be made without a tin catalyst so the composition may be tin free. Such urethane acrylic dispersions may be advantageously used as coatings for surfaces such as floors.

The PUD and urethanes of and/or used in the present invention are cross-linked (preferably at ambient temperature under standard conditions) by a Schiff base mechanism which means that crosslinking takes place by the reaction of a carbonyl functional group(s) (as defined herein) with a carbonyl-reactive amine and/or hydrazine (or blocked amine and/or blocked hydrazine) functional group. In this context ''carbonyl functional group‘ means an aldo or keto group and includes enolic carbonyl groups such as found in acetoacetyl groups. Suitable carbonyl-reactive compounds may comprise Schiff bases (or precursors therefor) which are compounds comprising at least one functional group with a carbon-nitrogen double bond where the nitrogen atom is connected to an aryl and/or alkyl group (and not hydrogen), such as stable imines for example compounds having the general formula R’R’’C=NR’’’ where R’, R’’ and R’’’ are independently organic moieties. Useful Schiff bases comprise azomethine and secondary aldimines (azomethines where the carbon is connected to a hydrogen atom, i.e. of general formula R’CH=NR’’) and/or Schiff bases derived from aniline, where R’’ is a phenyl or a substituted phenyl such compounds also referred to as anils. Schiff base precursors denote any suitable compounds which under the reaction conditions described herein transform or react to form a Schiff base which is capable of undergoing Schiff base crosslinking as defined herein. Examples of carbonyl-reactive amine (or blocked amine) functional groups include any of the following compounds or groups: R-NH_2, R-O-NH_2, R-O-N=C<, R-NH-C(=O)-O-N=C< and/or R-NH-C(=O)-O-NH_2 where R is optionally substituted C_1 to C_{15}, preferably C_1 to C_{10} alkylene, optionally substituted alicyclic, optionally substituted aryl, and/or R may also be part of a polymer. Examples of carbonyl-reactive hydrazine (or blocked hydrazine) compounds or groups include R-NH-NH_2, R-C(=O)-NH-NH_2, R-C(=O)-NH-N=C<, R-NH-C(=O)-NH-NH_2 and/or R-NH-C(=O)-NH-N=C< where R is as described above.

Many other variations embodiments of the invention will be apparent to those skilled in the art and such variations are contemplated within the broad scope of the present invention.

Further aspects of the invention and preferred features thereof are given in the claims herein.

Examples

The present invention will now be described in detail with reference to the following non limiting examples which is by way of illustration only.

Abbreviations:
DMPA = dimethylolpropionic acid
MMA = methyl methacrylate
n-BA = n-butylacrylate
BMA = butyl methacrylate
EDTA = ethylenediamine tetraacetic acid

Viscosity was determined with a Brookfield DV-I viscometer (spindle S61, 60 rpm, 23°C)

Particle size distribution was measured on a Particle Size Distribution Analyser (PSDA) from Polymer Laboratories. Samples are diluted until a concentration of approximately 0,05%. Samples are filtered over 2 micron filtered and measured on Cartridge Type 2 (20nm to 1500nm).

Reagents and materials:

- PL-PSDA Eluent concentrate: 0.04% Sodium azide solution (Polymer Laboratories part no. 0850- 2000, 4x 100ml)
- PL-PSDA Marker: 0.02 g 3-nitrobenzene sulfonic acid in 250ml Ultra pure water.
- Standards: Latex Particle Size Standards from 2-1000 nm; KSTN0026, KSTN 0027, KSTN0028 and KSTN0033 t/m KSTN0039

- Ultra pure demineralized water or HPLC grade water.
- Syringe filters: regenerated cellulose, 0.45μm membrane, Spartac Millex-AP 20 pre filter 25 MM, 2.0μm membrane, Millipore.

For determining the particle size value, the median diameter is mentioned in the examples. When a broad particle size distribution is found, the diameter at peak value is mentioned.

Comparative Example Comp A (reproduced from example XI of US 2010/009867 (Da Costa))

A reaction vessel, equipped with internal thermometer, stirrer and cooler, was filled, under nitrogen atmosphere and at room temperature, with 442.6 g of polypropylene ether glycol (having molecular weight 2,000 g/mol), 30.9 g of DMPA and 50.0 g of N-methylpyrrolidone. The mixture was heated to 40 °C and stirred for 30 minutes. 213.2 g Desmodur W (available from Bayer) was added under stirring to the homogeneous mixture which was then heated to 60°C for 30 minutes. The reaction temperature was brought to 100°C and maintained for 2 hours, until the titrimetric determination of the free NCO groups still present gave a calculated value of 4.12% by weight. 650 g of the obtained prepolymer, cooled to 65°C, are dispersed in 10 minutes under vigorous stirring into 1057.1 g of demineralised water cooled at 18°C and containing 10.84 g of potassium hydroxide. Then 65.2 g of a 15.5% aqueous solution of hydrazine are added in 10 minutes and a maximum temperature of 34°C is reached during the extension step. After 30 minutes stirring, the NCO peak in the IR spectrum at 2240 cm^{-1} is disappeared and 1.780 g of BYK® 346 are added. The resulting amine free (but N-methyl pyrrolidone containing) polyurethane dispersion had a solids content of 34.3 wt %, a pH of 8.0 and a viscosity of 66 cps. The median particle size was 170 nm.

Example 1

PEC-205 is a ketone-functional polyester polyol, available from DSM, which has a hydroxyl value of 80 mg KOH/g and an acid value of < 1 mg KOH/g. The ketone functionality is 1.7 milliequivalents carbonyl groups per g polyol. A 2000 cm^3 flask equipped with a thermometer and overhead stirrer was charged with 144.12 g of polyol PEC-205, 76.37 g polyTHF 650 (OH-value = 173.5 mg KOH/g), 231.18 g Desmodur W (available from Bayer), 29.64 g DMPA, 69.42 g MMA and 0.11 g butylated hydroxytoluene. This mixture was heated to 50°C and tin octoate (0.20 g) was added. The reaction was allowed to exotherm to 90° C. After the exotherm was complete the reaction was kept at 90° C for 2 hours. The isocyanate content of the prepolymer was 6.54% (theoretical 6.72%). Then 540.0 g of the obtained prepolymer was cooled to a temperature of 40°C and 191.41 g of a 5.68% KOH solution in demineralized water was added under vigorous stirring. Subsequently 704.14 g of demineralized water was added to the flask and the mixture was stirred until a homogeneous dispersion was obtained. After that, 71.37 g of a 15.5% hydrazine solution was added together with 34.0 g of water. The radical polymerization was initiated by the addition of 0.48 g of tertiary butyl hydroperoxide in demineralized water, 0.011 g of iron(II)EDTA and a subsequent feed addition of 17.0 g of a 1% solution of isoascorbic acid in demineralized water, over a period of 10 minutes. Finally, 15.29 g of adipic acid dihydrazide and 4.14 g of BYK®-346 were added. The batch was filtered through a filter cloth to remove any coagulum formed during the reaction. The resulting amine free polyurethane acrylic hybrid dispersion had a solids content of 35.7 wt %, a pH of 7.5 and a viscosity of 36 cps. The median particle size was 47 nm.

Comparative Example Comp B

A 2000 cm^3 flask equipped with a thermometer and overhead stirrer was charged with 99.66 g polypropylene glycol 1000 (OH-value = 112 mg KOH/g), 137.82 g polypropylene glycol 2000 (OH-value = 56 mg KOH/g), 172.48 g Desmodur W (available from Bayer), 21.58 g DMPA, 107.88 g MMA and 0.17 g butylated hydroxytoluene. This mixture was heated to 50°C and tin octoate (0.11 g) was added. The reaction was allowed to exotherm to 90° C. After the exotherm was complete the reaction was kept at 90° C for 2 hours. The isocyanate content of the prepolymer was 4.99% (theoretical 5.12%).

528.23 g of the obtained prepolymer was cooled to a temperature of 40°C and 186.65 g of a 5.68% KOH solution in demineralized water was added under vigorous stirring.

Subsequently 744.78 g of demineralized water was added to the flask and the mixture was stirred until a homogeneous dispersion was obtained. After that, 53.19 g of a 15.5% hydrazine solution was added together with 17.6 g of water.

The radical polymerization was initiated by the addition of 0.74 g of tertiary butyl hydroperoxide, 0.02 g of iron(II)EDTA and a subsequent feed addition of 26.4 g of a 1% solution of isoascorbic acid in demineralized water, over a period of 10 minutes.

The batch was filtered through a filter cloth to remove any coagulum formed during the reaction. The resulting amine free polyurethane acrylic hybrid dispersion had a solids content of 34.3 wt %, a pH of 7.7 and a viscosity of 15 cps. The median particle size was 59 nm.

Example 2

PEC-205 is a ketone-functional polyester polyol, available from DSM, which has a hydroxyl value of 80 mg KOH/g and an acid value of < 1 mg KOH/g. The ketone functionality is 1.7 milliequivalents carbonyl groups per g polyol.

A 2000 cm^3 flask equipped with a thermometer and overhead stirrer was charged with 237.48 g of polyol PEC-205, 172.48 g Desmodur W (available from Bayer), 21.58 g DMPA, 107.88 g MMA and 0.17 g butylated hydroxytoluene. This mixture was heated to 50°C and tin octoate (0.11 g) was added. The reaction was allowed to exotherm to 90° C. After the exotherm was complete the reaction was kept at 90° C for 2 hours. The isocyanate content of the prepolymer was 4.83% (theoretical 5.12%).

526.9 g of the obtained prepolymer was cooled to a temperature of 40°C and 186.17 g of a 5.68% KOH solution in demineralized water was added under vigorous stirring.

Subsequently 742.9 g of demineralized water was added to the flask and the mixture was stirred until a homogeneous dispersion was obtained. After that, 53.05 g of a 15.5% hydrazine solution was added together with 17.6 g of water.

The radical polymerization was initiated by the addition of 0.64 g of tertiary butyl hydroperoxide, 0.02 g of iron(II)EDTA and a subsequent feed addition of 26.33 g of a 1% solution of isoascorbic acid in demineralized water, over a period of 10 minutes. Finally, 25.10 g of adipic acid dihydrazide was added.

The batch was filtered through a filter cloth to remove any coagulum formed during the reaction. The resulting amine free polyurethane acrylic hybrid dispersion had a solids content of 34.3 wt %, a pH of 7.3 and a viscosity of 1995 cps. The median particle size was 56 nm.

Example 3

PEC-205 is a ketone-functional polyester polyol, available from DSM, which has a hydroxyl value of 80 mg KOH/g and an acid value of < 1 mg KOH/g. The ketone functionality is 1.7 milliequivalents carbonyl groups per g polyol. A 2000 cm^3

flask equipped with a thermometer and overhead stirrer was charged with 660.37 g of polyol PEC-205, 479.63 g Desmodur W (available from Bayer), 60.0 g DMPA, 300.0 g MMA and 0.30 g butylated hydroxytoluene. This mixture was heated to 50°C and tin octoate (0.35 g) was added. The reaction was allowed to exotherm to 90° C. After the exotherm was complete the reaction was kept at 90° C for 2 hours. The isocyanate content of the prepolymer was 4.97% (theoretical 5.13%). Then 600.0 g of the obtained prepolymer was cooled to a temperature of 40°C and 170.4 g of a 5.89% KOH solution in demineralized water was added under vigorous stirring. Subsequently 891.0 g of demineralized water was added to the flask and the mixture was stirred until a homogeneous dispersion was obtained. After that, 65.96 g of a 15.5% hydrazine solution was added together with 10.0 g of water. The radical polymerization was initiated by the addition of 0.25 g of tertiary butyl hydroperoxide, 0.012 g of iron(II)EDTA and a subsequent feed addition of 14.4 g of a 2.5% solution of isoascorbic acid in demineralized water, over a period of 10 minutes. The batch was mixed for 10 minutes at 45°C and subsequently was cooled to 25°C. Then 476.0 g of this urethane/acrylic hybrid dispersion was diluted with 150 g of demineralized water and 70.66 g of n-butyl acrylate and 29.44 g of methyl methacrylate were added to the mixture, which was then stirred for one hour. After that, 0.3 g of tertiary butyl hydroperoxide were added and a second radical polymerization of the (meth)acrylic monomers was initiated by a feed addition of 12.0 g of a 1% solution of isoascorbic acid in demineralized water, over a period of 10 minutes. After completion of the reaction, 8.52 g of adipic acid dihydrazide and 25.6 g of demineralized water were added. The batch was filtered through a filter cloth to remove any coagulum formed during the reaction. The pH of the resultant composition was about 7. The resulting amine free polyurethane acrylic hybrid dispersion had a solids content of 35 wt %. The acid value of the dispersion is 10.5 mg KOH/ g solid resin. Urethane/acrylic ratio is 50/50 and theoretical value of the overall Tg of the acrylic phase is 0°C.

The resulting amine free polyurethane acrylic hybrid dispersion had a solids content of 34.2 wt %, a pH of 6.9 and a viscosity of 10 cps. The median particle size was 65 nm.

Example 4

A polyester polyol was synthesized from the following components: Pripol 1009 (available from Croda, 49 wt%), adipic acid (12 wt%) and 1,4 cyclohexane dimethanol (39 wt%). The polyester polyol had a hydroxyl value of 113 mg KOH/g and an acid value of 0.47 mg KOH/g. A 2000 cm^3 flask equipped with a thermometer and overhead stirrer was charged with 324.87 g of this polyester polyol, 253.51 g Desmodur W (available from Bayer), 21.0 g DMPA, 150.04 g MMA and 0.35 g butylated hydroxytoluene. This mixture was heated to 50°C and tin octoate (0.35 g) was added. The reaction was allowed to exotherm to 90° C. After the exotherm was complete the reaction was kept at 90° C for 2 hours. The isocyanate content of the prepolymer was 5.23% (theoretical 5.42%). Then 332.9 g of the obtained prepolymer was cooled to a temperature of 40°C and 82.40 g of a 5.68% KOH solution in demineralized water and 8.14 g of Antarox CA-630 were added under vigorous stirring. Subsequently 521.7 g of demineralized water was added to the flask and the mixture was stirred until a homogeneous dispersion was obtained. After that, 39.88 g of a 15.5% hydrazine solution was added together with 20.49 g of water. Subsequently 0.82 g of Tego foamex 805, 294.47 g of demineralized water, 54.2316 g of n-butyl acrylate, 127.19 g of methyl methacrylate and 23.46 g of butyl methacrylate were added and the mixture was stirred for one hour. After that, 2.36 g of tertiary butyl hydroperoxide and 0.03 g of iron(II)EDTA were added. The radical polymerization of the (meth)acrylic monomers was initiated by a feed addition of 67.9 g of a 1% solution of isoascorbic acid in demineralized water, over a period of 10 minutes. Then 400.0 g of this dispersion was used for a next radical polymerization step. To this amount, 57.0 g of demineralized water, 23.8 g of methyl methacrylate, 9.71 g of n-butyl acrylate and 1.04 g of diacetone acrylamide were added and the mixture was stirred for one hour. After that, 0.104 g of tertiary butyl hydroperoxide and 0.004 g of iron(II)EDTA were added. The radical polymerization of the (meth)acrylic monomers was initiated by a feed addition of 2.76 g of a 2 % solution of isoascorbic acid in demineralized water, over a period of 10 minutes. Finally, 0.38 g of adipic acid dihydrazide were added to the dispersion.

The batch was filtered through a filter cloth to remove any coagulum formed during the reaction. The resulting amine free polyurethane acrylic hybrid dispersion had a solids content of 34.8 wt %, a pH of 7.9 and a viscosity of 12 cps.

Example 5

PEC-205 is a ketone-functional polyester polyol, available from DSM, which has a hydroxyl value of 80 mg KOH/g and an acid value of < 1 mg KOH/g. The ketone functionality is 1.7 milliequivalents carbonyl groups per g polyol. A 2000 cm^3 flask equipped with a thermometer and overhead stirrer was charged with 144.12 g of polyol PEC-205, 76.37 g polyTHF 650 (OH-value = 173.5 mg KOH/g), 231.18 g Desmodur W (available from Bayer), 29.64 g DMPA, 69.42 g MMA and 0.11 g butylated hydroxytoluene. This mixture was heated to 50°C and tin octoate (0.20 g) was added. The reaction was allowed to exotherm to 90° C. After the exotherm was complete the reaction was kept at 90° C for 2 hours. The isocyanate content of the prepolymer was 6.54% (theoretical 6.72%). Then 540.0 g of the obtained prepolymer was cooled to a temperature of 40°C and 191.41 g of a 5.68% KOH solution in demineralized water was added under vigorous stirring. Subsequently 704.14 g of demineralized water was added to the flask and the mixture was stirred until a homogeneous dispersion was obtained. After that, 71.37 g of a 15.5% hydrazine solution was added together with 34.0 g of water. The radical polymerization was initiated by the addition of 0.48 g of tertiary butyl hydroperoxide in demineralized water, 0.011 g of of iron(II)EDTA and a subsequent feed addition of 17.0 g of a 1% solution of isoascorbic acid in demineralized water, over a period of 10 minutes. Finally, 4.14 g of BYK®-346 were added. 200.0 g of this dispersion was used for a next radical polymerization step. To this amount, 153.3 g of demineralized water, 58.76 g of methyl methacrylate, 23.96 g of n-butyl acrylate and 2.56 g of diacetone acrylamide were added and the mixture was stirred for one hour. After that, 0.26 g of tertiary butyl hydroperoxide and 0.008 g of iron(II)EDTA were added. The radical polymerization of the (meth)acrylic monomers was initiated by a feed addition of 6.82 g of a 2 % solution of isoascorbic acid in demineralized water, over a period of 10 minutes. Finally, 2.86 g of adipic acid dihydrazide were added to the dispersion. The batch was filtered through a filter cloth to remove any coagulum formed during the reaction. The resulting amine free polyurethane acrylic hybrid dispersion had a solids content of 34.2 wt %, a pH of 7.8 and a viscosity of 19 cps..

Table 1: Formulations

Example	Coalescent	BYK-346	Film appearance
Comp A	None	None	Good
Ex 1	10% Dowanol DPM	0.25%	Good
Comp B	1% Dowanol DPnB	0.25%	Good
Ex 2	10% Dowanol DPnB	0.25%	Good
Ex 3	10% Dowanol DPnB	0.25%	Good
Ex 4	12% Dowanol DPM	0.50%	Good
Ex 5	10% Dowanol DPM	0.25%	Good

Formulations were prepared by slow addition of the additives (mentioned in the Table above) to the polyurethane dispersion, while stirring.

Stain Resistance

The examples, prepared and formulated as described above were cast onto a Leneta test chart using a wire rod at a wet film thickness of 125 micron. The cast films were then allowed to dry at room temperature for 1 hour, followed by ageing of the coatings at 50°C for 16 hours. The coatings were allowed to cool to room temperature for 1 hour.

The stain resistance of the coated cards towards the following stains were then assessed: water, ethanol (48%), detergent (Andy, 50% solution), coffee, hot pan. In all cases, a spot (1 cm^2) of the respective stain was placed on the coating and covered with a piece of filter paper and a watch glass. In case of the “hot pan test” a small glass beaker filled with boiling hot water was placed on cold water on a test chart. All mentioned spots were left for one hour; water, ethanol (48%) and detergent (50%) were also tested for 16 hours. After these periods, the spot was gently wiped off with a tissue and the film was assessed for its integrity. This was rated between 0 to 5, where 0 = film totally destroyed/strongly discoloured and 5 = film fully intact without any defects/discolouration. The results for the clear coatings are shown in Tables 2A and 2B below.

Table 2A: Properties

Ex.	Hardness	Resistances 1h				
		W	E48%	A50%	C	HP
A	36	1	0	1	2	0
1	121	5	4	5	4	5
B	68	2	1	2	2	2
2	85	5	4-5	5	4-5	4
3	87	5	4	5	4-5	4-5
4	102	5	3-4	5	5	2
5	113	5	2	5	5	4-5

Table 2B: Properties (continued)

Ex.	Resistances 16h				Total score
	W	E48%	A50%	C	
A	0	0	1	1	6
1	5	0-1	4-5	2	35
B	2	0-1	3	1	15.5
2	5	4	5	3-4	40.5
3	5	5	5	2	40
4	5	3	4-5	5	38
5	5	1	4-5	4-5	36.5

Hardness = König hardness (seconds)

W = water

E48% = ethanol, 48% solution in demineralized water

A50% = Andy, 50% solution in demineralized water (detergent)

C = coffee

HP = hot pan

Total score = sum of all individual scores on stain resistances

CLAIMS

1 A process for preparing a Schiff base crosslinkable aqueous dispersion of a polyurethane A the process comprising the steps of:

(a) reacting the following components one to four (two and four where present) to form an acidic isocyanate terminated prepolymer that comprises anionic or potentially anionic functional groups thereon; where:

(1) component one comprises 10 to 80% by weight of at least one polyisocyanate optionally containing at least one anionic or potentially anionic dispersing group;

(2) optional component two comprises up to 15% by weight of at least one isocyanate-reactive polyol containing at least one anionic or potentially anionic dispersing group;

(3) component three comprises 15 to 85% by weight of at least one isocyanate reactive polyol other than component two if present, and having a weight average molecular weight greater than or equal to 500 Daltons optionally containing at least one anionic or potentially anionic dispersing group; and

(4) optional component four comprises up to 20% by weight of at least one isocyanate reactive polyol other than component three and two if present and having a weight average molecular weight less than 500 Daltons;

where if component two is not present component one or three comprise at least one anionic or potentially anionic dispersing group;

where the amounts of components one to four are expressed as a weight percentage calculated from the total amount of the above components (i.e. one and three and optional two and/or four where present) being 100%; and where the mixture used in step (a) is substantially free of volatile amines and N-alkyl pyrrolidinones;

(b) adding to the reaction mixture from step (a) an alkali metal neutralising agent in an amount from 0.05 to 6 parts by weight substantially to neutralise the isocyanate terminated prepolymer obtained from step (a);

where the amount (in weight parts) of the alkali metal neutralising agent is calculated based on the weight of alkali metal in the neutralising agent relative to the total amount of components one to four in step (a) being equal to 100 parts; and

(c) reacting the neutralised prepolymer from step (b) with an active hydrogen compound to extend the chain of the prepolymer to form an aqueous dispersion of polyurethane A

2 A process as claimed in claim 1, in which polyurethane A and/or vinyl polymer B are Schiff base cross-linkable under ambient conditions.

3 A process as claimed in either preceding claim, in which either component one two or three comprises at least one anionic or potentially anionic dispersing group.

4 A process as claimed in any preceding claim, in which step (a) comprises:

(a) reacting:

- (1) 10 to 80% by weight of at least one polyisocyanate;
- (2) 1 to 15% by weight of at least one isocyanate-reactive polyol containing at least one anionic or potentially anionic dispersing group;
- (3) 15 to 85% by weight of at least one isocyanate reactive polyol other than (2), and having a weight average molecular weight $\geq$ 500 Daltons; and
- (4) optionally up to 20% by weight of at least one isocyanate reactive polyol other than (2) and (3) and having a weight average molecular weight < 500 Dalton;

to form an acidic isocyanate terminated prepolymer that comprises anionic or potentially anionic functional groups and which is substantially free of volatile amines and N-alkyl pyrrolidinones. and

(ii) 90 to 5% by weight of a vinyl polymer B wherein the weight % amounts of (i) and (ii) are calculated as a percentage of the total amount of (i) and (ii) and these percentages add up to 100%; and

where the composition is:

substantially free of volatile amines and N-alkyl pyrrolidinones (preferably solvent free); and

is neutralised with a metal neutralising agent and the composition comprises a polyamine of polyhydrazide compound.

5 A process as claimed in any preceding claim, in which step (b) occurs during or substantially immediately after step (a).

6. An aqueous dispersion of a polyurethane A obtained and/or obtainable by a process as claimed any preceding claim.

7 A process for preparing an aqueous coating composition comprising bringing into intimate admixture components (i) and (ii): where

(i) component (i) comprises 10% to 95% by weight of a polyurethane dispersion A as claimed claim 6; and

(ii) component (ii) comprises 90% to 5% by weight of a vinyl polymer B optionally with a glass transition temperature $\geq$ 15°C, where

the weight % amounts of components (i) and (ii) are calculated as a percentage of the total amount of (i) and (ii) and these percentages add up to 100%;

and where the composition:

is substantially free of volatile amines and N-alkyl pyrrolidinones (preferably solvent free);

is neutralised with a metal neutralising agent; and

comprises a polyamine of polyhydrazide compound.

8. An aqueous coating composition comprising a polyurethane A and a vinyl polymer B, obtained and/or obtainable by a process as claimed in claim 6.

9 An aqueous coating composition comprising:

(i) 10 to 95% by weight of a polyurethane A obtained by the reaction of:

(a) an isocyanate terminated prepolymer formed from components one to five comprising:

(1) 10 to 80 parts by weight of at least one polyisocyanate

(2) 1 to 15 parts by weight of at least one isocyanate-reactive polyol containing at least one anionic or potentially anionic dispersing group

(3) 15 to 85 parts by weight of at least one isocyanate reactive polyol other than (2) of weight average molecular weight $\geq$ 500 Daltons

(4) optionally up to 20 parts by weight of at least one isocyanate reactive polyol other than (2) or (3) of weight average molecular weight < 500 Daltons

(5) 0.05 to 6 parts by weight of an alkali metal neutralising agent (preferably whose cation acts as counterion of the anionic group of (1), (2) or (3)).

where the amounts of (1), (2), (3), (4) and (5) are calculated as a weight parts relative to the total amount of components (1) to (5) being 100 weight parts.

(b) an active hydrogen chain extending compound; and

(ii) 90 to 5% by weight of an ambient self cross-linkable vinyl polymer B wherein the weight % amounts of (i) and (ii) are calculated as a percentage of the total amount of (i) and (ii) and these percentages add up to 100%; and

where the composition is:

substantially free of volatile amines and N-alkyl pyrrolidinones (preferably solvent free); and is neutralised with a metal neutralising agent and the composition comprises a polyamine of polyhydrazide compound.

10. An article and/or substrate coated by a composition as claimed in claim 8 or 9.

11. A method of coating an article and/or substrate comprising the steps of

(I) applying a coating composition as claimed in claim 8 or 9 to an article and/or substrate, and

(II) drying the coating thereon to obtain a coated article and/or substrate.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/057455

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/08 C08G18/12 C09D175/14 C08G18/32
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/074541 A1 (DSM IP ASSETS BV [NL]; SATGURUNATHAN RAJASINGHAM [NL]; ROELANDS MARC [) 18 June 2009 (2009-06-18) page 6, line 26 - line 27; claim 1; example 1 -----	1-11
X	WO 2005/023947 A1 (AVECIA BV [NL]; AVECIA LTD [GB]; SATGURUNATHAN RAJASINGHAM [NL]; MARTI) 17 March 2005 (2005-03-17) page 4, line 39; claims 1-24; example 1 -----	1-11
X	WO 2006/002865 A1 (DSM IP ASSETS BV [NL]; VAN CASTEREN ILSE [NL]; ROELANDS MARC [NL]; OVE) 12 January 2006 (2006-01-12)	1-11
Y	claim 2; examples I-II ----- -/--	1-11

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2009/105396 A1 (LUBRIZOL ADVANCED MAT INC [US]; PAJERSKI ANTHONY D [US]; LERNER SVETLA) 27 August 2009 (2009-08-27) paragraphs [0038] - [0045] paragraphs [0046] - [0077] paragraph [0085] -----	1-11
Y	US 5 623 016 A (KLEIN HEINZ-PETER [DE] ET AL) 22 April 1997 (1997-04-22) column 3, line 41 - column 4, line 8; example 2 -----	1-11

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/057455

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009074541 A1	18-06-2009	CN 101945906 A	12-01-2011
		EP 2222743 A1	01-09-2010
		US 2011020556 A1	27-01-2011
		US 2013129927 A1	23-05-2013
		WO 2009074541 A1	18-06-2009
WO 2005023947 A1	17-03-2005	EP 1664220 A1	07-06-2006
		US 2006258801 A1	16-11-2006
		WO 2005023947 A1	17-03-2005
WO 2006002865 A1	12-01-2006	CN 1980965 A	13-06-2007
		EP 1761578 A1	14-03-2007
		HK 1107652 A1	18-05-2012
		US 2007260022 A1	08-11-2007
		WO 2006002865 A1	12-01-2006
WO 2009105396 A1	27-08-2009	AU 2009215691 A1	27-08-2009
		CN 101959916 A	26-01-2011
		EP 2247633 A1	10-11-2010
		JP 2011512445 A	21-04-2011
		US 2011009561 A1	13-01-2011
		WO 2009105396 A1	27-08-2009
US 5623016 A	22-04-1997	AT 176678 T	15-02-1999
		AU 677427 B2	24-04-1997
		BR 9404213 A	04-07-1995
		CA 2134043 A1	24-04-1995
		CZ 9402607 A3	17-05-1995
		DE 4336206 A1	27-04-1995
		DE 59407799 D1	25-03-1999
		DK 0649865 T3	20-09-1999
		EP 0649865 A1	26-04-1995
		ES 2127329 T3	16-04-1999
		FI 944925 A	24-04-1995
		HU 214037 B	29-12-1997
		JP 3834340 B2	18-10-2006
		JP 4361918 B2	11-11-2009
		JP H07233347 A	05-09-1995
		JP 2006299274 A	02-11-2006
		NO 944008 A	24-04-1995
		US 5571861 A	05-11-1996
		US 5623016 A	22-04-1997

(19) 中华人民共和国国家知识产权局

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权利要求书3页 说明书14页

(54) **发明名称**

聚合物、组合物和用途

(57) **摘要**

本发明描述了用于制备可Schiff碱交联的聚氨酯A的水性分散体(PUD)的工艺，该工艺包括：(a)使所存在的组分(1)至(4)反应，以形成酸性异氰酸酯封端的预聚物，该预聚物在其上包含阴离子或潜在阴离子官能基团；其中：(1)组分一包含10至80重量％的至少一种多异氰酸酯，其任选地包含至少一个阴离子或潜在阴离子分散基团；(2)任选的组分二包含至多15重量％的至少一种异氰酸酯反应性多元醇，其包含至少一个阴离子或潜在阴离子分散基团；(3)组分三包含15至85重量％的至少一种不同于存在的组分二的异氰酸酯反应性多元醇，其具有大于或等于500道尔顿的重均分子量，任选地包含至少一个阴离子或潜在阴离子分散基团；并且(4)任选的组分四包含至多20重量％的至少一种不同于组分三和存在的组分二的异氰酸酯反应性多元醇，其具有小于500道尔顿的重均分子量；其中如果组分二不存在，则组分一或组分三包含至少一个阴离子或潜在阴离子分散基团；其中组分一至组分四的量表示为上述组分（即组分一和三以及任选的组分二和／或组分四，如果存在的话）的总量（为100％）计算得到的重量百分数；并且其中步骤(a)中所使用的混合物基本上不含挥发性胺和N-烷基吡咯烷酮；(b)向来自步骤(a)的反应混合物中以0.05至6重量％的量添加碱金属中和试剂，来基本上中和由步骤(a)获得的异氰酸酯封端的预聚物；其中碱金属中和试剂的量（以重量份计）是相对于步骤(a)中组分一至四的总量（等于100份）基于中和试剂中碱金属的重量计算的；以及(c)使来自步骤(b)的经中和的预聚物与活性氢化合物反应，来扩展预聚物的链，以形成聚氨酯A的水性分散体。并且(ii)90至5重量％的乙烯基聚合物B，其中(i)和(ii)的重量％被计算为相对于(i)和(ii)的总量的百分数，这些百分数总和为100％；并且其中组合物：基本上不含挥发性胺和N-烷基吡咯烷酮（优选地不含溶剂）；是用金属中和试剂中和的，并且该组合物包含多酰肼化合物的多胺。本发明的另一个方面提供了通过上述工艺获得的水性涂料，其中聚氨酯A和／或乙烯基聚合物B在环境条件下可Schiff碱交联。

1. 制备可Schiff碱交联的聚氨酯A的水性分散体的工艺，所述工艺包括如下步骤：

(a)使如下组分一至四（如果存在组分二和四的话）反应，以形成酸性异氰酸酯封端的预聚物，该预聚物在其上包含阴离子或潜在阴离子官能基团；其中：

(1)组分一包含10至80重量％的至少一种多异氰酸酯，其任选地包含至少一个阴离子或潜在阴离子分散基团；

(2)任选的组分二包含至多15重量％的至少一种异氰酸酯反应性多元醇，其包含至少一个阴离子或潜在阴离子分散基团；

(3)组分三包含15至85重量％的至少一种不同于如果存在的组分二的异氰酸酯反应性多元醇，其具有大于或等于500道尔顿的重均分子量，任选地包含至少一个阴离子或潜在阴离子分散基团；并且

(4)任选的组分四包含至多20重量％的至少一种不同于组分三和如果存在的组分二的异氰酸酯反应性多元醇，其具有小于500道尔顿的重均分子量；

其中如果组分二不存在，则组分一或组分三包含至少一个阴离子或潜在阴离子分散基团；

其中组分一至组分四的量表示为由上述组分（即组分一和三以及任选的组分二和/或组分四，如果存在的话）的总量计算得到的重量百分数，上述组分的总量为100％；并且

其中步骤(a)中所使用的混合物基本上不含挥发性胺和N-烷基吡咯烷酮；

(b)向来自步骤(a)的反应混合物中以0.05至6重量％的量添加碱金属中和试剂，来基本上中和由步骤(a)获得的所述异氰酸酯封端的预聚物；

其中碱金属中和试剂的量（以重量份计）是相对于步骤(a)中组分一至四的总量基于中和试剂中碱金属的重量计算的，所述组分一至四的总量等于100份；以及

(c)使来自步骤(b)的经中和的预聚物与活性氢化合物反应，来扩展预聚物的链，以形成聚氨酯A的水性分散体。

2. 如权利要求1所述的工艺，其中聚氨酯A和/或乙烯基聚合物B是在环境条件下可Schiff碱交联的。

3. 如前面权利要求中任意一项所述的工艺，其中组分一、二或三中的任意组分包含至少一个阴离子或潜在阴离子分散基团。

4. 如前面权利要求中任意一项所述的工艺，其中步骤(a)包括：

(a)使以下物质反应：

(1)10至80重量％的至少一种多异氰酸酯；

(2)1至15重量％的至少一种异氰酸酯反应性多元醇，其含有至少一个阴离子或潜在阴离子分散基团；

(3)15至85重量％的至少一种不同于(2)的异氰酸酯反应性多元醇，其具有≥500道尔顿的重均分子量；并且

(4)任选地至多20重量％的至少一种不同于(2)和(3)的异氰酸酯反应性多元醇，其具有<500道尔顿的重均分子量；

以形成酸性异氰酸酯封端的预聚物，该预聚物包含阴离子或潜在阴离子官能基团并且基本上不含挥发性胺和N-烷基吡咯烷酮。以及

(ii)90至5重量％的乙烯基聚合物B，其中(i)和(ii)的重量％被计算为相对于(i)

和 (ii) 的总量的百分数，这些百分数总和为 100％；并且

其中组合物：

基本上不含挥发性胺和 N- 烷基吡咯烷酮（优选地不含溶剂）；并且

是用金属中和试剂中和的，并且所述组合物包含多酰肼化合物的多胺。

5. 如前面权利要求中任意一项所述的工艺，其中步骤 (b) 在步骤 (a) 发生时进行或者在步骤 (a) 后基本上立即进行。

6. 聚氨酯 A 的水性分散体，其通过前面权利村要求中任意一项所述的工艺获得和 / 或能够获得。

7. 用于制备水性涂料组合物的工艺，其包括直接混合组分 (i) 和 (ii)：其中

(i) 组分 (i) 包含 10 重量％至 95 重量％的权利要求 6 中所限定的聚氨酯分散体 A；并且

(ii) 组分 (ii) 包含 90 重量％至 5 重量％的乙烯基聚合物 B，其任选地具有≥ 15℃的玻璃化转变温度，其中

组分 (i) 和 (ii) 的重量％的量被计算为相对于 (i) 和 (ii) 的总量的百分数，这些百分数总和为 100％；

并且其中组合物：

基本上不含挥发性胺和 N- 烷基吡咯烷酮（优选地不含溶剂）；

是用金属中和试剂中和的，并且

包含多酰肼化合物的多胺。

8. 包含聚氨酯 A 和乙烯基聚合物 B 的水性涂料组合物，其通过权利要求 6 中所限定的工艺获得和 / 或能够获得。

9. 水性涂料组合物，其包含：

(i)10 至 95 重量％的聚氨酯 A，所述聚氨酯 A 通过如下物质 (a) 和 (b) 的反应获得：

(a) 由组分一至组分五形成的异氰酸酯封端的预聚物，其包含：

(1)10 至 80 重量份的至少一种多异氰酸酯；

(2)1 至 15 重量份的至少一种异氰酸酯反应性多元醇，其包含至少一个阴离子或潜在阴离子分散基团；

(3)15 至 85 重量份的至少一种不同于 (2) 的异氰酸酯反应性多元醇，其具有≥ 500 道尔顿的重均分子量；

(4) 任选地至多 20 重量份的至少一种不同于 (2) 或 (3) 的异氰酸酯反应性多元醇，其具有＜ 500 道尔顿的重均分子量；

(5)0.05 至 6 重量份的碱金属中和试剂（优选地其中的阳离子作为 (1)、(2) 或 (3) 的阴离子基团的抗衡离子）；

其中 (1)、(2)、(3)、(4) 和 (5) 的量被计算为相对于组分 (1) 至 (5) 的总量的重量份，所述组分 (1) 至 (5) 的总量为 100 重量份；

(b) 活性氢扩链化合物；和

(ii)90 至 5 重量％的可环境自交联的乙烯基聚合物 B，其中 (i) 和 (ii) 的重量％的量被计算为相对于 (i) 和 (ii) 的总量的百分数，并且这些百分数总和为 100％；并且

其中该组合物：

基本上不含挥发性胺和N-烷基吡咯烷酮（优选地不含溶剂）;并且是用金属中和试剂中和的,并且所述组合物包含多酰肼化合物的多胺。

10. 制品和/或基材,其由权利要求8或9中所限定的组合物涂布。

11. 用于涂布制品和/或基材的工艺,其包括如下步骤：

(I) 将权利要求8或9中所限定的涂料组合物涂覆到制品和/或基材上,并

(II) 使其上的涂料干燥,以获得经涂布的制品和/或基材。

聚合物、组合物和用途

[0001] 本发明涉及聚氨酯领域、尤其氨基甲酸酯－丙烯酸基分散体领域。

[0002] 氨基甲酸酯－丙烯酸(U-A)分散体对水、化学品、溶剂以及磨损具有良好耐性，因此通常用于涂料组合物诸如装饰性和保护性涂料中。

[0003] 为了制备稳定的水性氨基甲酸酯－丙烯酸分散体，丙烯酸部分和聚氨酯(PU)部分二者都必须分散于水中。这可以通过表面活性剂来部分地实现，以及通过在聚氨酯聚合物中引入合适的基团诸如离子或非离子亲水性基团（在聚合物链的侧链上或者在链中）来部分地实现。这种基团包括阴离子诸如羧酸、磺酸、硫酸酯或磷酸酯基团，这些阴离子通常通过如下引入到PU中：使含有反应性氢和至少一个合适的酸基团（通常羧酸）的化合物与多异氰酸酯反应以形成氨基甲酸酯－丙烯酸分散体的聚氨酯组分的。在所获得的分散体中保留大量的酸性材料是不期望的，因此最终产物中存在的酸的主要部分（如果不是所有的话）必须被中和。

[0004] 还期望减少或消除表面活性剂在水性涂料分散体中的使用，因为大量表面活性剂的使用会提高所形成的涂料的水敏感性。

[0005] 当添加简单的无机碱（例如KOH)来中和阴离子聚氨酯分散体以使其中的酸基团中和时，发现这些无机碱并不能满足要求。一般来说，当添加强的无机碱时，聚氨酯分散体的粘度会不期望地上升。为了防止分散体失去稳定性，可以使用大量亲水性基团诸如聚乙氧基基团改性聚氨酯。所获得的膜和涂料（无论PU是改性的或未改性的）也是高度水敏感性的（与用其他试剂中和的PUD相比），除非添加额外的试剂来交联聚氨酯。因此，其他中和试剂被用来制备可商业购得的PU分散体，最常见的为挥发性胺诸如叔胺三乙胺(TEA)。这些材料很容易获得并且易于从最终的膜蒸发。

[0006] 然而已知的是，挥发性胺还具有各种缺点。例如它们在膜形成时易于蒸发挥发性有机化合物(VOC)，引起不可接受的环境污染和／或当用于室内时引起差的室内空气质量。未来会更加严格地控制这种材料的使用。因此，期望的是，找到一种提供稳定的水性氨基甲酸酯－丙烯酸分散体的替代性工艺和／或在其制备时中和所使用的酸性材料的替代性工艺。

[0007] 已经提出了多种替代性方案来改善水性氨酸甲酸酯分散体的稳定性。

[0008] US 2968575描述了使用乳化剂而分散于水中的PU胶乳。

[0009] US 4501852描述了稳定的聚氨酯－脲的水性分散体，其包含(i)每100g中10-120meq的以化学方式引入其中的阴离子基团和(ii)至多约10重量％的包含环氧乙烷(EO)单元的亲水性链。为了抗衡阴离子基团，配制物包含以约1：4至4：1的当量比例的挥发性阳离子和非挥发性阳离子的混合物。其实施例使用OH数为26的正丁醇、环氧乙烷和环氧丙烷的非离子聚醚一元醇作为组分(ii)（摩尔比为83：17)。虽然该组分辅助了分散，但提高了水敏感性。其实施例还使用了不期望的NMP作为溶剂。

[0010] US 4701480描述了具有改善的水解稳定性的水性聚氨酯－脲分散体，其由含有羧酸基团水性聚氨酯－脲－分散体形成，该羧酸基团被挥发性有机碱中和，随后通过添加有机或无机酸的碱金属盐转化成非挥发性阳离子，其中碱金属盐的量使得足以替换至少一部分

挥发性有机碱。挥发性有机碱可以通过减压蒸馏来任选地去除。所有实施例均包含NMP，蒸馏是不期望的，因为其消耗大量能量且会引起过量的泡沫形成（如US2010/0099967在对比例XVI中的描述）。

[0011]　US 2006-0229409描述了由TMXDI制成的聚氨酯分散体，其中在第9页的具体实施方式中提到了使用金属氢氧化物。这并未在实施例中给出实例，TMXDI也不是用于涂料中的合适的二异氰酸酯（太软）。

[0012]　US 2010-0098867(Costa)描述制备羧化阴离子聚氨酯的水性分散体的工艺，该阴离子聚氨酯不含挥发性胺并且不包含任何聚氧乙烯或聚氧丙烯侧链。首先，预聚物（包含2-10重量%异氰酸酯基团和10-100meq的羧酸基团）是通过如下反应制备的：使具有羧酸基团的多元醇、非离子多元醇和脂（环）族多异氰酸酯反应。将预聚物分散在碱金属氢氧化物的水性溶液中，然后用多胺使预聚物扩链。

[0013]　EP1153051描述了具有侧链羧酸基团的阴离子聚氨酯的水性分散体，其中羧酸基团被反应性挥发性胺化合物（叔氨官能的丙烯酸单体(DMAEMA)）中和，之后该化合物通过自由基聚合被引入到聚合物骨架中。未反应的游离单体保持在最终产物中，因此最终产物仍然包含挥发性胺。单体还可以包含单体中的杂质，并且水解会产生不期望的副产物二甲基乙醇胺。

[0014]　WO93/24551描述了水性聚氨酯聚合物分散体，其包含以下物质的反应产物：有机多异氰酸酯；聚酯多元醇；和活性氢链扩展化合物，所述聚酯多元醇中包含由二聚酸获得的聚合单元、非离子和/或离子分散基团和至少一个如下聚合单元：分子量(Mw)＜400的脂环族多元醇、MW＜400的脂环族多元酸、MW＜500的芳族多元醇、Mw＜500的芳族二酸。

[0015]　WO 2001-027179(Stahl)描述了阴离子聚氨酯分散体，其被叔胺官能的氨基甲酸酯聚合物或低聚物中和。尽管聚合材料比诸如TEA的试剂具有较少的挥发性，但是这种工艺使PU分散体的制备增加了额外的费用和复杂性，并且在去除所有酸性基团方面并非完全成功。

[0016]　本申请人已经惊奇地发现稳定丙烯酸酯与阴离子聚氨酯的水性分散体的工艺，该工艺不具有前述缺点。

[0017]　具体来说，申请人已经发现了，在工艺的早期阶段添加碱金属中和试剂会减小或避免现有技术中存在的一些或所有前述问题。

[0018]　因此，本发明广义地包含用于制备聚氨酯[A]的水性分散体的工艺，该工艺包括如下步骤：

[0019]　(a)将组分一和组分三（以及存在的组分二和组分四）反应，以形成酸性异氰酸酯封端的预聚物，该预聚物在其上包含阴离子或潜在阴离子官能基团；其中：

[0020]　(1)组分一包含10至80重量%的至少一种多异氰酸酯，其任选地包含至少一个阴离子或潜在阴离子分散基团；

[0021]　(2)任选的组分二包含至多15重量%的至少一种异氰酸酯反应性多元醇，其包含至少一个阴离子或潜在阴离子分散基团；

[0022]　(3)组分三包含15至85重量%的至少一种不同于如果存在的组分二的异氰酸酯反应性多元醇，其具有大于或等于500道尔顿的重均分子量，任选地包含至少一个阴离子或潜在阴离子分散基团；并且

[0023] (4) 任选的组分四包含至多 20 重量%的至少一种不同于组分三和如果存在的组分二之外的异氰酸酯反应性多元醇，其具有小于 500 道尔顿的重均分子量；

[0024] 其中如果组分二不存在，则组分一或组分三包含至少一个阴离子或潜在阴离子分散基团；

[0025] 其中组分一至组分四的量表示为上述组分（即组分一和三以及任选的组分二和/或组分四，如果存在的话）的总量（为 100%）计算得到的重量百分数；并且

[0026] 其中步骤 (a) 中所使用的混合物基本上不含挥发性胺和 N-烷基吡咯烷酮；

[0027] (b) 向来自步骤 (a) 的反应混合物中以 0.05 至 6 重量%的量添加碱金属中和试剂，来基本上中和由步骤 (a) 获得的异氰酸酯封端的预聚物；

[0028] 其中碱金属中和试剂的量（以重量份计）是相对于步骤 (a) 中组分一至四的总量（等于 100 份）基于中和试剂中碱金属的重量计算的；并且

[0029] (c) 将来自步骤 (b) 的经中和的预聚物与活性氢化合物反应，来扩展预聚物的链，以形成聚氨酯 A 的水性分散体。

[0030] 可以看出，(a) 和 (b) 一起给出的各成分的量的总和总计大于 100 重量份。

[0031] 在本发明的工艺中，任意组分 (1)(2) 和/或 (3)（即任意的它们自身或任意组合）可以包含至少一个阴离子或潜在阴离子分散基团。然而，优选的是，异氰酸酯组分 (1) 不包含阴离子或潜在阴离子分散基团，而是至少一个这种基团构成多元醇组分 (2)。

[0032] 因此，在本发明的工艺的一个实施方式中，步骤 (a) 包括：

[0033] (a) 使以下物质反应：

[0034] (1)10 至 80 重量%的至少一种多异氰酸酯；

[0035] (2)1 至 15 重量%的至少一种异氰酸酯反应性多元醇，其含有至少一个阴离子或潜在阴离子分散基团；

[0036] (3)15 至 85 重量%的至少一种不同于 (2) 的异氰酸酯反应性多元醇，其具有≥ 500 道尔顿的重均分子量，任选地包含至少一个阴离子或潜在阴离子分散基团；并且

[0037] (4) 任选地至多 20 重量%的至少一种不同于 (2) 和 (3) 的异氰酸酯反应性多元醇，其具有＜ 500 道尔顿的重均分子量；

[0038] 以形成酸性异氰酸酯封端的预聚物，该预聚物包含阴离子或潜在阴离子官能基团并且基本上不含挥发性胺和 N-烷基吡咯烷酮（例如 TEA、NMP 或 NEP）。

[0039] 优选地，步骤 (b) 在步骤 (a) 发生时进行或者在步骤 (a) 后基本上立即进行。

[0040] 不受任何机理限制，据信在步骤 (b) 中来自碱金属中和试剂的金属阳离子形成预聚物上的阴离子基团（和/或由预聚物上的潜在阴离子基团形成的阴离子基团）的抗衡离子。

[0041] 本发明的另一个方面提供了用于制备水性涂料组合物的工艺，其包括直接混合 (intimate admixture) 组分 (i) 和 (ii)：

[0042] (i)10 重量%至 95 重量%、优选地 20 重量%至 80 重量%、更优选地 30 重量%至 65 重量%的聚氨酯分散体 A，其通过本文中所描述的本发明的工艺获得和/或能够获得；和

[0043] (ii)90 重量%至 5 重量%、优选地 80 重量%至 20 重量%、更优选地 70 重量%至 35 重量%的乙烯基聚合物 B，其任选地具有≥ 15℃的玻璃化转变温度

[0044] 其中

[0045] (i) 和 (ii) 总和为 100％并且是基于固体（排除水）的重量计算的 ;并且

[0046] 其中该组合物（以及组分 (i) 与组分 (ii) 二者）基本上不含挥发性胺和 N- 烷基吡咯烷酮。

[0047] 优选地，组分 (i) 与 (ii) 二者均形成存在于相同颗粒中的不同相。

[0048] 优选地，在如上所述的本发明的工艺中，在环境条件下，聚氨酯 A 和 / 或乙烯基聚合物 B 是可自交联的、优选地可 Schiff 碱交联的。更优选地，聚氨酯 A 包含能够进行 Schiff 碱自交联的羰基。

[0049] 本发明的另外还有一个方面提供了通过本发明的工艺获得和 / 或能够获得的水性涂料组合物。

[0050] Schiff 碱交联剂的用途已被描述为用于制备聚氨酯泡沫。例如 US4016113 描述了使用某些芳族或螺环二胺 Schiff 碱来交联 PU 泡沫。PU 泡沫的 Schiff 碱交联已经描述于 US3321433、US3657192、US3890255、US3907721 和 US3926867 中。

[0051] 然而，聚氨酯泡沫与水性 PU 分散体不同，尤其与氨基甲酸酯丙烯酸分散体不同，其中还没有使用 Schiff 碱来改善稳定性。令人惊奇的是，Schiff 碱交联反应仍然在碱性环境下进行。这是因为氨基甲酯丙烯酸分散体通常是碱性的，但在干燥后（随着胺蒸发）变为酸性的，而且据信低 pH（酸性条件）对于自交联来说是必需的。在一个体系中，例如本文中所描述的本发明的那些体系（其是永久碱性的）中，预期不会进行 Schiff 碱交联。

[0052] 例如，参见 Journal of Applied Polymer Science 第 104 卷，第 3948 页，2007 :“酸条件对于双丙酮丙烯酰胺与己二酸二酰肼之间的交联反应来说是不可缺少的。丙烯酸通常被引入到共聚物中，来提供酸条件，以促进交联反应”(‘Acid condition is indispensable for the crosslinking reaction between diacetone acrylamide and adipic acid dihydrazide.Acrylic acid is usually incorporated into copolymer to give an acid condition to facilitate the crosslinking reaction.’)（第 3948 页，第 2 栏第 26 至 33 行）。

[0053] 还参见 Journal Coat Technol.Res 5(3)p285(2008)，在讨论部分中“酮 - 酰肼交联的机理”记载了 :“在不同条件下反应的初始速率的比较清楚地表明化学反应速率随着 pH 降低而增加，如图 4 中所示。我们的结论是 :该反应是酸催化的”（‘Comparison of the initial rates of the reactions under different pH conditions clearly shows that the chemical reaction rate increases with decreasing pH,as illustrated in Fig.4.We conclude then that the reaction is acid catalysed.’)（第 288 页第 2 栏第 27 至 31 行）。标题为“结论”的部分中记载了 :“此外，交联反应是酸催化的并且反应速率随着 pH 降低而增加（“Conclusions”Moreover, the crosslinking reaction is acid catalysed and the reaction rate increases as pH decreases.’)（第 296 页第 1 栏第 21 至 23 行）。

[0054] 可以看出，对于在非酸性（中和的）或碱性体系中使用 Schiff 碱交联的丙烯酸聚合物存在技术偏见。本领域公知的是，PU 分散体是酸性的，必须被中和（出于本文中所描述的原因)，Schiff 碱交联从未被用在永久的碱性体系中。

[0055] 本申请人惊奇地发现，氨酸甲酸酯丙烯酸体系在永久被碱中和后仍然可以经由 Schiff 碱机理进行自交联。具体来说，本申请人发现，随后被中和的这些酸性水性 PU 分散

体可以包含可Schiff碱交联的氨基甲酸酯和/或乙烯基聚合物，用来生产氨基甲酸酯丙烯酸分散体，从而减少了或避免了现有技术中一些或所有前述问题的。

[0056] 因此，广义地，本发明的提供了水性涂料组合物，其包含：

[0057] (i)10至95重量%的可Schiff碱交联的聚氨酯A，该聚氨酯A通过如下物质的反应获得：

[0058] (a)由组分一至组分五形成的异氰酸酯封端的预聚物，所述组分包含：

[0059] (1)10至80重量份的至少一种多异氰酸酯；

[0060] (2)1至15重量份的至少一种异氰酸酯反应性多元醇，其包含至少一个阴离子或潜在阴离子分散基团；

[0061] (3)15至84重量份的至少一种不同于(2)的异氰酸酯反应性多元醇，其具有≥500道尔顿的重均分子量；任选地包含至少一个阴离子或潜在阴离子分散基团；

[0062] (4)任选地至多20重量份的至少一种不同于(2)或(3)的异氰酸酯反应性多元醇，其具有<500道尔顿的重均分子量；

[0063] (5)0.05至6重量份的碱金属中和试剂(优选地其中的阳离子作为(2)的阴离子基团的抗衡离子)；

[0064] 其中(1)、(2)、(3)、(4)和(5)的量被计算为相对于组分(1)至(5)的总量(为100重量份)的重量份。组分3和/或4包含可Schiff碱交联的羰基基团；

[0065] (b)活性氢扩链化合物；和

[0066] (ii)90至5重量%的含有可Schiff碱交联的羰基基团的乙烯基聚合物B，其中(i)和(ii)的重量%的量被计算为相对于(i)和(ii)的总量的百分数，并且这些百分数总和为100%；并且

[0067] 其中该组合物：

[0068] 基本上不含挥发性胺和N-烷基吡咯烷酮(优选地不含溶剂)；并且

[0069] 是用金属中和试剂中和的，并且组合物包含多酰肼化合物的多胺(apolyamine of polyhydrazide compound)。

[0070] 或者，本发明提供了水性涂料组合物，其包含：

[0071] (i)10至95重量%的可Schiff碱交联的聚氨酯A，该聚氨酯A通过如下物质的反应获得：

[0072] (a)由组分一至组分五形成的异氰酸酯封端的预聚物，所述组分包含：

[0073] (1)10至80重量份的至少一种多异氰酸酯；

[0074] (2)1至15重量份的至少一种异氰酸酯反应性多元醇，其包含至少一个阴离子或潜在阴离子分散基团；

[0075] (3)15至84重量份的至少一种不同于(2)的异氰酸酯反应性多元醇，其具有≥500道尔顿的重均分子量；任选地包含至少一个阴离子或潜在阴离子分散基团；

[0076] (4)任选地至多20重量份的至少一种不同于(2)或(3)的异氰酸酯反应性多元醇，其具有<500道尔顿的重均分子量；

[0077] (5)0.05至6重量份的碱金属中和试剂(优选地其中的阳离子作为(2)的阴离子基团的抗衡离子)；

[0078] 其中(1)、(2)、(3)、(4)和(5)的量被计算为相对于组分(1)至(5)的总量(为

100 重量份）的重量份。组分 3 和 / 或 4 包含可 Schiff 碱交联的羰基基团；

[0079] (b) 活性氢扩链化合物；和

[0080] (ii) 90 至 5 重量％的乙烯基聚合物 B，其中 (i) 和 (ii) 的重量％的量被计算为 (i) 和 (ii) 的总量的百分数，并且这些百分数总和为 100％；并且

[0081] 其中该组合物：

[0082] 基本上不含挥发性胺和 N- 烷基吡咯烷酮（优选地不含溶剂）；并且

[0083] 是用金属中和试剂中和的，并且组合物包含多酰肼化合物的多胺。

[0084] 或者，本发明提供了水性涂料组合物，其包含：

[0085] (i) 10 至 95 重量％的聚氨酯 [A]，该聚氨酯 A 通过如下物质的反应获得：

[0086] (a) 由组分一至组分五形成的异氰酸酯封端的预聚物，所述组分包含：

[0087] (1) 10 至 80 重量份的至少一种多异氰酸酯；

[0088] (2) 1 至 15 重量份的至少一种异氰酸酯反应性多元醇，其包含至少一个阴离子或潜在阴离子分散基团；

[0089] (3) 15 至 84 重量份的至少一种不同于 (2) 的异氰酸酯反应性多元醇，其具有 ≥ 500 道尔顿的重均分子量；任选地包含至少一个阴离子或潜在阴离子分散基团；

[0090] (4) 任选地至多 20 重量份的至少一种不同于 (2) 或 (3) 的异氰酸酯反应性多元醇，其具有＜ 500 道尔顿的重均分子量；

[0091] (5) 0.05 至 6 重量份的碱金属中和试剂（优选地其中的阳离子作为 (2) 的阴离子基团的抗衡离子）；

[0092] 其中 (1)、(2)、(3)、(4) 和 (5) 的量被计算为相对于组分 (1) 至 (5) 的总量（为 100 重量份）的重量份；

[0093] (b) 活性氢扩链化合物；和

[0094] (ii) 90 至 5 重量％的含有可 Schiff 碱交联的羰基基团的乙烯基聚合物 B，

[0095] 其中 (i) 和 (ii) 的重量％的量被计算为相对于 (i) 和 (ii) 的总量的百分数，并且这些百分数总和为 100％；并且

[0096] 其中该组合物：

[0097] 基本上不含挥发性胺和 N- 烷基吡咯烷酮（优选地不含溶剂）；并且是用金属中和试剂中和的，并且组合物包含多酰肼化合物的多胺。

[0098] 本发明的另一个方面提供了紧接上文所要求保护的水性涂料，其中聚氨酯 A 和 / 或乙烯基聚合物 B 在环境条件下是可 Schiff 碱交联的。

[0099] 如下组分可以优选地以如下的重量量存在，该重量量以相对于所存在的组分 (1) 至 (5) 的总量的重量份或重量百分数给出。

[0100] 优选地，组分 (1)（多异氰酸酯）以按重量计 15 至 70、更优选地 20 至 60、最优选地 25 至 50 的量存在。

[0101] 优选地，组分 (2)（阴离子异氰酸酯反应性多元醇）以按重量计 2 至 12、更优选地 3 至 10、最优选地 4 至 7 的量存在。

[0102] 优选地，组分 (3)（高 Mw（＞ 500D) 的异氰酸酯反应性多元醇）以按重量计 20 至 80、更优选地 25 至 75、最优选地 30 至 60 的量存在。

[0103] 优选地，任选组分 (4)（低 Mw（＜ 500D) 的异氰酸酯反应性多元醇）以按重量计

0.5 至 20、更优选地 1 至 15、最优选地 2 至 10 的量存在。

[0104] 优选地，任选组分 (5)（碱金属中和试剂）以按重量计 0.1 至 6、更优选地 0.2 至 5、最优选地 0.5 至 4 的量存在。

[0105] 术语“碱金属中和试剂”指的是碱金属化合物、优选地碱金属盐，其在多个条件（在该条件下制备聚氨酯分散体）下是足够碱性的，以中和聚合物上的酸性基团。不期望受任何机理限制，据信来自碱金属中和试剂的离子作为由聚合物上酸性基团所形成的离子基团的抗衡离子。优选的碱金属盐包含阳离子诸如钾、钠和 / 或锂，其中钠是更优选的。优选的碱金属盐包含阴离子诸如碳酸根、碳酸氢根、氢氧根和 / 或氢根，其中氢氧根是更优选的。最优选的碱金属中和试剂是氢氧化钠和 / 或氢氧化钾。

[0106] 本发明的聚氨酯分散体可以（除本文中另有指明外）使用常规的多元醇和异氰酸酯制备。

[0107] 例如，本发明中用作组分一的多异氰酸酯可以选自 WO2007-006586 中作为多异氰酸酯组分 (i) 所描述的那些（参见第 7 页第 33 行至第 8 页第 20 行，该部分段落通过引用并入本文）。

[0108] 例如，本发明中用作组分二、三和四的 NCO 反应性多元醇（满足本文中所指明的这些组分的其他要求）可以选自 WO2007-006586 中作为组分 (ii)、(iii) 和 / 或 (iv) 所描述的那些（参见第 8 页第 30 行至第 9 页第 24 行，该部分段落通过引用并入本文）。

[0109] 术语“可环境自交联的”是指聚合物在环境条件下会在不同的聚合物链上的不同官能基团之间形成共价键，以形成交联，而不需要添加额外的单独的交联剂。优选的自交联氨基甲酸酯 - 丙烯酸聚合物是带有羰基官能基团和羰基反应性胺和 / 或肼官能基团的那些，从而赋予氨基甲酸酯 - 丙烯酸聚合物可交联能力。优选地，聚氨酯 [A] 或乙烯基聚合物 [B] 能够通过在环境条件下的 Schiff 碱反应来进行自交联（也被称为 Schiff 碱交联）。或者，聚氨酯 A 和乙烯基聚合物 B 二者均能够通过在环境条件下 Schiff 碱反应来进行自交联。

[0110] 不期望受任何机理限制，据信在 Schiff 碱交联中，羰基和 (C ＝ O 反应性) 胺 / 肼基团一起在 Schiff 碱反应中反应，以使聚合物链连接。羰基可以通过至少一种含羰基的单烯属不饱和单体（例如双丙酮二丙烯酰胺 (DAAM)）的自由基加成聚合来被引入到乙烯基聚合物中。羰基反应性胺和 / 或酰肼基团可以通过多胺和 / 或多酰肼化合物（例如己二酸二酰肼）的加成来引入。类似地，可以使用羰基官能组分 (3)，来在聚氨酯中引入可 Schiff 碱反应的基团。

[0111] 组分一包含多异氰酸酯。合适的多异氰酸酯可以包括通过引入氨基甲酸酯、脲基甲酸酯、脲、缩二脲、碳化二亚胺、脲酮亚胺、脲二酮 (urethdione) 或异氰酸酯片段而改性的脂族、脂环族、芳脂族、芳族和 / 或多异氰酸酯。合适的多异氰酸酯的实例包括亚乙基二异氰酸酯 (ethylene diisocyanate)、1,6- 六亚甲基二异氰酸酯、异佛尔酮二异氰酸酯、1,4- 环己基二异氰酸酯、4,4’ - 二环己基甲烷二异氰酸酯、对苯二甲基二异氰酸酯、α，α’ - 四甲基二甲苯二异氰酸酯、1,4- 对苯二异氰酸酯、2,4- 甲苯二异氰酸酯、2,6- 甲苯二异氰酸酯、4,4’ - 二苯基甲烷二异氰酸酯、聚亚甲基聚亚苯基多异氰酸酯 (polymethylene polyphenyl polyisocyanate)、2,4’ - 二苯基甲烷二异氰酸酯、3(4)- 异氰酸根合甲基 -1- 甲基环己基异氰酸酯 (3(4)-isocyanatomethyl-1-methyl cyclohexyl isocyanate)、1,5- 萘二异氰酸酯及其混合物。优选的多异氰酸酯是异佛尔酮二异氰酸酯、4,4' - 二环己基甲烷二异氰酸酯、甲苯二异氰酸酯和 4,4' - 二苯基甲烷二异氰酸酯。

[0112] 组分二、三和四包含本文中所限定各种多元醇。合适的多元醇可以包括丙二醇、聚（环氧丙烷 / 环氧乙烷）共聚物、聚四氢呋喃、聚丁二烯、氢化聚丁二烯、聚硅氧烷、聚酰胺聚酯、异氰酸酯反应性聚氧乙烯化合物、聚酯、聚醚、聚醚酯、聚己内酯、聚硫醚、聚碳酸酯、聚醚碳酸酯、聚缩醛和聚烯烃多元醇。

[0113] 优选的组分二包含在其上具有阴离子或潜在阴离子分散基团的多元醇。

[0114] 优选的阴离子分散基团是羧酸、磷酸、膦酸或磺酸基团。优选的潜在阴离子分散基团是本文中所描述的阴离子分散基团的前体，即在步骤 (a) 的条件下会转变成阴离子分散基团的基团。最优选的阴离子分散基团是羧酸或磺酸基团。通过在步骤 (a) 中使用碱金属中和试剂中和阴离子基团，来实现到盐形式的转化。

[0115] 组分三包含重均分子量大于 500 道尔顿的异氰酸酯反应性多元醇（高 mw 多元醇）。组分四包含重均分子量小于 500 道尔顿的异氰酸酯反应性多元醇。

[0116] 在聚氨酯 A 是可 Schiff 碱交联的情况下，优选地组分 3 包含适用于 Schiff 碱交联的羰基。组分 3 的端基含量为 0.1-10meq 羰基 / 克多元醇、优选地 0.5-5meq 羰基 / 克多元醇、最优选地 1-3meq 羰基 / 克多元醇。

[0117] 在本发明的实施例中，羰基（即醛或酮）官能基团的存在可以通过任何合适的已知方法确定，例如通过在 ^{13}C nmr 谱中 ^{13}C 共振的方式。对于酮和醛羰基来说，不考虑侧链取代基的情况下，这些羰基碳通常出现在 190 至 210ppm。这些碳可以与来自其他 C = O 基团的碳 13 共振区分开，其他 C = O 基团诸如羧酸衍生物（酰胺、酯、羧酸、酰氯等）通常出现在 160 至 185ppm。例如，在一种合适的方法中，可以记录 200mg 样品在 600 微升 $CDCl_3$ 与乙酰丙酮铬 (III)（也称为 $Cr(acac)_3$) 的载体介质中的 ^{13}C NMR 谱。或者，在本发明的工艺中，羰基（即醛或酮）的存在可以从反应混合物的远红外谱中的相关吸收峰来确定。从这些已知工艺或其他已知工艺，可以测定样品中存在的未反应的羰基基团的量。

[0118] 在聚乙烯基聚合物 B 是可 Schiff 碱交联的情况下，乙烯基聚合物包含适用于 Schiff 碱交联的羰基。优选地，乙烯基聚合物包含基于总单体的 0.1-20 重量％的羰基官能单体、更优选地基于总单体的 0.5-10 重量％的羰基官能单体、最优选地基于总单体的 1-5 重量％的羰基官能单体。

[0119] 优选地，胺基团与羰基基团的当量比为 0.2 至 1.5、更优选地 0.35 至 1.1、最优选地 0.6 至 0.9。

[0120] 在本发明的一个实施方式中，优选地，本发明的和 / 或根据本发明的工艺制备的丙烯酸氨基甲酸酯基本上不含任何非离子官能的多元醇，因为相信这种组分会使耐水性恶化。

[0121] 在本发明的另外还有一个实施方式中，优选地，本发明的或者在本发明中制备的聚氨酯分散体 (PUD) 和 / 或氨基甲酸酯丙烯酸化合物是永久碱性的（即用碱金属中和试剂中和后），优选地展现出＞ 8 的 pH。尽管认为，具有高 pH 的 PUD 和氨基甲酸酯丙烯酸涂料是不期望的，但申请人已经惊奇地发现它们可以解决本文中所指明的一些或所有问题。

[0122] 任选地，可以添加额外的表面活性剂，来促进氨基甲酸酯的分散，然而这是不优选的，因为它会对耐水性产生不利影响。

[0123] 在本发明中，优选地，向预聚物中添加中和试剂，因为通过预先中和预聚物可以合成具有较低酸值的氨基甲酸酯，其具有改善的耐水性。更优选地，添加水性溶液形式的中和试剂。

[0124] 本发明的优选组合物具有低酸值（AV），更优选地总组合物的 AV 为 1 至 40mg KOH/g、更优选地 2-20mg KOH/g、最优选地 3-15mg KOH/g。

[0125] 不期望受任何机理限制，据信经（碱）金属离子中和的氨基甲酸酯 - 丙烯酸基分散体包含足够的可环境自交联基团，来补偿恶化的耐化学污染性、尤其耐水性，并且任选地还可以在没有锡催化剂的存在下来制备，因此这样的组合物可以不含锡。这种氨基甲酸酯丙烯酸分散体可以有利地用作用于诸如地板的表面的涂料。

[0126] 本发明的 PUD 和氨基甲酯和 / 或本发明中所使用的 PUD 和氨基甲酸酯是通过 Schiff 碱机理交联的（优选地在环境温度下在标准条件下），这意味着交联通过羰基官能基团（如本文中所限定）与羰基反应性胺和 / 或肼（或封端的胺和 / 或封端的肼）官能基团的反应来进行。在上下文中，“羰基官能基团”指的是醛或酮基团并且包括烯醇羰基，例如发现于乙酰乙酰基团中。合适的羰基反应性化合物可以包括 Schiff 碱（或其前体），其为包含至少一个具有碳 - 氮双键的官能基团的化合物，其中氮原子与芳基和 / 或烷基（非氢）相连，例如稳定的亚胺，诸如具有通式 R’R”C ＝ NR”’ 的化合物，其中 R’、R”和 R”’ 独立地为有机片段。有用的 Schiff 碱包含偶氮甲碱 (azomethine) 和仲醛亚胺 (secondary aldimine)（偶氮甲碱中碳与氢原子相连，即具有通式 R’CH ＝ NR′ ’）和 / 或衍生自苯胺的 Schiff 碱，其中 R”是苯或取代的苯，这种化合物也被称为苯氨衍生物 (anils)。Schiff 碱前体表示在本文中所描述的反应条件下会转变或反应形成能够进行本文中所定义的 Schiff 碱交联的 Schiff 碱的任何合适化合物。羰基反应性胺（或封端的胺）官能基团的例子包括任意如下化合物或基团：R-NH$_2$、R-O-NH$_2$、R-O-N ＝ C ＜、R-NH-C（＝ O）-O-N ＝ C ＜和 / 或 R-NH-C（＝ O）-O-NH$_2$，其中 R 为任选地被取代的 C$_1$ 至 C$_{15}$、优选地 C$_1$ 至 C$_{10}$ 亚烃基、任选地被取代的脂环族、任选地被取代的芳基，和 / 或 R 还可以是聚合物的一部分。羰基反应性肼（或封端的肼）化合物或基团的例子包括 R-NH-NH$_2$、R-C（＝ O）-NH-NH$_2$、R-C（＝ O）-NH-N ＝ C ＜、R-NH-C（＝ O）-NH-NH$_2$ 和 / 或 R-NH-C（＝ O）-NH-N ＝ C ＜，其中 R 如上所述。

[0127] 本发明的许多其他变型实施方式对本领域技术人员来说是显而易见的，并且这些变型包含在本发明的宽范围内。

[0128] 在本文中的权利要求书中给出本发明的其他方面及其优选特征。

实施例

[0129] 现将参考如下非限制性实施例来详细描述本发明，这些实施例仅仅是说明性的。

[0130] 简写：

[0131] DMPA ＝二羟甲基丙酸

[0132] MMA ＝甲基丙烯酸甲酯

[0133] n-BA ＝丙烯酸正丁酯

[0134] BMA ＝甲基丙烯酸丁酯

[0135] EDTA ＝乙二胺四乙酸

[0136] 粘度是用 Brookfield DV-I 粘度计（spindle S61，60rpm，23℃）测定的。

[0137] 颗粒尺寸分布是在来自Polymer Laboratories的Particle Size Distribution Analyser(PSDA)上测定的。将样品稀释，直到浓度大约为0.05％。将样品滤过2微米的过滤器并在Cartridge Type 2(20nm至1500nm)上测定。

[0138] 试剂和材料：

[0139] -PL-PSDA洗脱浓缩液：0.04％叠氮化钠溶液(Polymer Laboratories part no.0850-2000，4x 100ml)

[0140] -PL-PSDA Marker：0.02g 3-硝基苯磺酸在250ml超纯水中。

[0141] -标准品：2-1000nm的乳胶颗粒尺寸标准品；KSTN0026，KSTN0027，KSTN0028和KSTN0033t/m KSTN0039

[0142] -超纯净去离子水或HPLC级水。

[0143] -针头式过滤器：再生纤维素，0.45μm膜，Spartac Millex-AP 20预过滤器25毫米，2.0μm膜，微孔。

[0144] 为了测定颗粒尺寸值，在实施例中提到中值直径。当发现宽的颗粒尺寸分布时，提到峰值处直径。

[0145] 对比例Comp A(由US 2010/009867(Da Costa)的实施例XI再现)

[0146] 在氮气气氛下在室温下，用442.6g聚亚丙基醚二醇(具有2000g/mol的分子量)、30.9g的DMPA和50.0g的N-甲基吡咯烷酮填充配备有内部温度计、搅拌器和冷却器的反应容器。将混合物加热到40℃并搅拌30分钟。在搅拌下向均匀混合物中添加213.2g Desmodur W(可从Bayer获得)，之后将其加热至60℃ 30分钟。将反应温度升高到100℃并保持2小时，直到仍然存在的游离NCO基团的滴定法测定结果给出4.12重量％的计算值。将650g的所获得的预聚物冷却至65℃，并在剧烈搅拌下在10分钟内分散到1057.1g的在18℃冷却的去矿物质水中，该去矿物质水包含10.84g的氢氧化钾。然后，在10分钟内添加65.2g的15.5％肼的水溶液，并且在扩链步中最高温度达到34℃。搅拌30分钟后，IR谱中在2240cm^{-1}处的NCO峰消失了，然后添加1.780g的BYK® 346。所获得的不含胺(但含有N-甲基吡咯烷酮)的聚氨酯分散体的固体含量为34.3重量％，pH为8.0并且粘度为66cps。中值颗粒尺寸为170nm。

[0147] 实施例1

[0148] PEC-205是酮官能的聚酯多元醇，可从DSM获得，其具有80mgKOH/g的羟值和＜1mg KOH/g的酸值。酮官能度为1.7毫当量羰基每g多元醇。用144.12g多元醇PEC-205、76.37g聚四氢呋喃650(OH-值＝173.5mg KOH/g)、231.18g Desmodur W(可从Bayer获得)、29.64g DMPA、69.42g MMA和0.11g丁基化的羟基甲苯填充配备有温度计和顶部搅拌器的2000cm^{3}烧瓶。将该混合物加热至50℃，并且添加辛酸亚锡(0.20g)。反应放热至90℃。放热结束后，将反应保持在90℃下2个小时。预聚物的异氰酸酯含量为6.54％(理论值6.72％)。然后，将540.0g所获得的预聚物冷却至40℃的温度，并在剧烈搅拌下添加191.41g的KOH在去矿物质水中的5.68％溶液。接下来，向烧瓶中添加704.14g的去矿物质水，并搅拌混合物，直到获得均匀分散体。之后，添加71.37g的15.5％肼溶液和34.0g的水。通过在10分钟的时间段中添加在去矿物质水中的0.48g的叔丁基氢过氧化物、0.011g铁(II)EDTA并随后添加17.0g的异抗坏血酸在去矿物质水中的1％溶液，来引发自由基聚合。最后，添加15.29g己二酸二酰肼和4.14g的BYK®-346。将该批料通过滤布过滤，以去除反应时形

成的任何凝固物。所获得的不含胺的聚氨酯丙烯酸混杂分散体的固体含量为35.7重量%，pH为7.5并且粘度为36cps。中值颗粒尺寸为47nm。

[0149] 对比例Comp B

[0150] 用99.66g聚丙二醇1000(OH-值＝112mg KOH/g)、137.82g聚丙二醇2000(OH-值＝56mg KOH/g)、172.48g Desmodur W(可从Bayer获得)、21.58g DMPA、107.88g MMA和0.17g丁基化的羟基甲苯填充配备有温度计和顶部搅拌器的2000cm^{3}烧瓶。将该混合物加热至50℃，并且添加辛酸亚锡(0.11g)。反应放热至90℃。放热结束后，将反应保持在90℃下2个小时。预聚物的异氰酸酯含量为4.99%(理论值5.12%)。

[0151] 将528.23g所获得的预聚物冷却至40℃的温度，并在剧烈搅拌下添加186.65g的在去矿物质水中的5.68% KOH溶液。

[0152] 接下来，向烧瓶中添加744.78g的去矿物质水，并搅拌混合物，直到获得均匀分散体。之后，添加53.19g的15.5%肼溶液和17.6g的水。

[0153] 通过在10分钟的时间段中添加0.74g叔丁基氢过氧化物、0.02g铁(II)EDTA并随后添加26.4g的异抗坏血酸在去矿物质水中的1%溶液，来引发自由基聚合。

[0154] 将该批料通过滤布过滤，以去除反应时形成的任何凝固物。所获得的不含胺的聚氨酯丙烯酸混杂分散体的固体含量为34.3重量%，pH为7.7并且粘度为15cps。中值颗粒尺寸为59nm。

[0155] 实施例2

[0156] PEC-205是酮官能的聚酯多元醇，可从DSM获得，其具有80mg KOH/g的羟值和＜1mg KOH/g的酸值。酮官能度为1.7毫当量羰基每g多元醇。

[0157] 用237.48g多元醇PEC-205、172.48g Desmodur W(可从Bayer获得)、21.58g DMPA、107.88g MMA和0.17g丁基化的羟基甲苯填充配备有温度计和顶部搅拌器的2000cm^{3}烧瓶。将该混合物加热至50℃，并且添加辛酸亚锡(0.11g)。反应放热至90℃。放热结束后，将反应保持在90℃下2个小时。预聚物的异氰酸酯含量为4.83%(理论值5.13%)。

[0158] 将526.9g所获得的预聚物冷却至40℃的温度，并在剧烈搅拌下添加186.17g的在去矿物质水中的5.68% KOH溶液。

[0159] 接下来，向烧瓶中添加742.9g的去矿物质水，并搅拌混合物，直到获得均匀分散体。之后，添加53.05g的15.5%肼溶液和17.6g的水。

[0160] 通过在10分钟的时间段中添加0.64g叔丁基氢过氧化物、0.02g铁(II)EDTA并随后添加26.33g的异抗坏血酸在去矿物质水中的1%溶液，来引发自由基聚合。最后，添加25.10g己二酸二酰肼。

[0161] 将该批料通过滤布过滤，以去除反应时形成的任何凝固物。所获得的不含胺的聚氨酯丙烯酸混杂分散体的固体含量为34.3重量%，pH为7.3并且粘度为1995cps。中值颗粒尺寸为56nm。

[0162] 实施例3

[0163] PEC-205是酮官能的聚酯多元醇，可从DSM获得，其具有80mg KOH/g的羟值和＜1mg KOH/g的酸值。酮官能度为1.7毫当量羰基每g多元醇。用660.37g多元醇PEC-205、479.63g Desmodur W(可从Bayer获得)、60.0g DMPA、300.0g MMA和0.30g丁基化的羟基甲苯填充配备有温度计和顶部搅拌器的2000cm^{3}烧瓶。将该混合物加热至50℃，并且添加

辛酸亚锡(0.35g)。反应放热至90℃。放热结束后,将反应保持在90℃下2个小时。预聚物的异氰酸酯含量为4.97%(理论值5.13%)。将600.0g所获得的预聚物冷却至40℃的温度,并在剧烈搅拌下添加170.4g的在去矿物质水中的5.89% KOH溶液。接下来,向烧瓶中添加891.0g的去矿物质水,并搅拌混合物,直到获得均匀分散体。之后,添加65.96g的15.5%肼溶液和10.0g的水。通过在10分钟的时间段中添加0.25g叔丁基氢过氧化物、0.012g铁(II)EDTA并随后添加14.4g的异抗坏血酸在去矿物质水中的2.5%溶液,来引发自由基聚合。将该批料在45℃下混合10分钟,然后冷却至25℃。然后,用150g去矿物质水稀释476.0g的此氨基甲酸酯/丙烯酸混杂分散体,并向混合物中添加70.66g丙烯酸正丁酯和29.44g甲基丙烯酸甲酯,然后搅拌一个小时。之后,添加0.3g叔丁基氢过氧化物,并且通过在10分钟的时间段中添加12.0g的异抗坏血酸在去矿物质水中的1%溶液,来引发(甲基)丙烯酸单体的第二自由基聚合。反应完成后,添加8.52g己二酸二酰肼和25.6g去矿物质水。将该批料通过滤布过滤,以去除反应时形成的任何凝固物。所获得的组合物的pH约为7。所获得的不含胺的聚氨酯丙烯酸混杂分散体的固体含量为35重量%。分散体的酸值为10.5mg KOH/g固体树脂。氨基甲酸酯/丙烯酸比例为50/50,并且丙烯酸相的整体Tg的理论值为0℃。

[0164] 所获得的不含胺的聚氨酯丙烯酸混杂分散体的固体含量为34.2重量%,pH为6.9并且粘度为10cps。中值颗粒尺寸为65nm。

[0165] 实施例4

[0166] 由下列组分合成聚酯多元醇:Pripol 1009(可从Croda获得,49重量%)、己二酸(12重量%)和1,4环己烷二甲醇(39重量%)。聚酯多元醇具有113mg KOH/g的羟值和0.47mg KOH/g的酸值。用324.87g该聚酯多元醇、253.51g Desmodur W(可从Bayer获得)、21.0g DMPA、150.04g MMA和0.35g丁基化羟基甲苯填充配备有温度计和顶部搅拌器的$2000cm^3$烧瓶。将该混合物加热至50℃,并且添加辛酸亚锡(0.35g)。反应放热至90℃。放热结束后,将反应保持在90℃下2个小时。预聚物的异氰酸酯含量为5.23%(理论值5.42%)。然后将332.9g所获得的预聚物冷却至40℃的温度,并在剧烈搅拌下添加82.40g的在去矿物质水中的5.68% KOH溶液和8.14g的Antarox CA-630。接下来,向烧瓶中添加521.7g的去矿物质水,并搅拌混合物,直到获得均匀分散体。之后,添加39.88g的15.5%肼溶液和20.49g的水。随后添加0.82g的Tego foamex805、294.47g去矿物质水、54.2316g丙烯酸正丁酯、127.19g甲基丙烯酸甲酯和23.46g甲基丙烯酸丁酯,并将混合物搅拌一个小时。之后,添加2.36g叔丁基氢过氧化物和0.03g铁(II)EDTA。通过在10分钟的时间段中添加67.9g的异抗坏血酸在去矿物质水中的1%溶液,来引发(甲基)丙烯酸单体的自由基聚合。然后,将400.0g该分散体用于接下来的自由基聚合步骤。向此量中,添加57.0g去矿物质水、23.8g甲基丙烯酸甲酯、9.71g丙烯酸正丁酯和1.04g双丙酮丙烯酰胺,并将混合物搅拌一个小时。之后,添加0.104g叔丁基氢过氧化物和0.004g铁(II)EDTA。通过在10分钟的时间段中添加2.76g的异抗坏血酸在去矿物质水中的2%溶液,来引发(甲基)丙烯酸单体的自由基聚合。最后,向分散体添加0.38g己二酸二酰肼。

[0167] 将该批料通过滤布过滤,以去除反应时形成的任何凝固物。所获得的不含胺的聚氨酯丙烯酸混杂分散体的固体含量为34.8重量%,pH为7.9,并且粘度为12cps。

[0168] 实施例5

[0169] PEC-205是酮官能的聚酯多元醇，可从DSM获得，其具有80mg KOH/g的羟值和＜1mg KOH/g的酸值。酮官能度为1.7毫当量羰基每g多元醇。用144.12g多元醇PEC-205、76.37g聚四氢呋喃650（OH-值＝173.5mg KOH/g）、231.18g Desmodur W（可从Bayer获得）、29.64g DMPA、69.42g MMA和0.11g丁基化羟基甲苯填充配备有温度计和顶部搅拌器的2000cm^{3}烧瓶。将该混合物加热至50℃，并且添加辛酸亚锡（0.20g）。反应放热至90℃。放热结束后，将反应保持在90℃下2个小时。预聚物的异氰酸酯含量为6.54%（理论值6.72%）。然后将540.0g所获得的预聚物冷却至40℃的温度，并在剧烈搅拌下添加191.41g的在去矿物质水中的5.68% KOH溶液。接下来，向烧瓶中添加704.14g的去矿物质水，并搅拌混合物，直到获得均匀分散体。之后，添加71.37g的15.5%肼溶液和34.0g的水。通过在10分钟的时间段中添加0.48g在去矿物质水中的叔丁基氢过氧化物、0.011g铁(II)EDTA并随后添加17.0g的异抗坏血酸在去矿物质水中的1%溶液，来引发自由基聚合。最后，添加4.14g的BYK® -346。将200.0g该分散体用于接下来的自由基聚合步骤。向此量中，添加153.3g去矿物质水、58.76g甲基丙烯酸甲酯、23.96g丙烯酸正丁酯和2.56g双丙酮丙烯酰胺，并将混合物搅拌一个小时。之后，添加0.26g叔丁基氢过氧化物和0.008g铁(II)EDTA。通过在10分钟的时间段中添加6.82g的异抗坏血酸在去矿物质水中的2%溶液，来引发（甲基）丙烯酸单体的自由基聚合。最后，向分散体添加2.86g己二酸二酰肼。将该批料通过滤布过滤，以去除反应时形成的任何凝固物。所获得的不含胺的聚氨酯丙烯酸混杂分散体的固体含量为34.2重量%，pH为7.8，并且粘度为19cps。

[0170] 表1：配制物

[0171]

实例	凝结剂	BYK-346	膜外观
Comp A	无	无	良好
实施例1	10% Dowanol DPM	0.25%	良好
Comp B	1% Dowanol DPnB	0.25%	良好
实施例2	10% Dowanol DPnB	0.25%	良好
实施例3	10% Dowanol DPnB	0.25%	良好
实施例4	12% Dowanol DPM	0.50%	良好
实施例5	10% Dowanol DPM	0.25%	良好

[0172] 在搅拌下，通过向聚氨酯分散体中缓慢添加添加剂（如上表中所提到）来制备配制物。

[0173] 耐污性

[0174] 使用线棒以125微米的湿膜厚度将如上所述制备和配制的实例浇铸到Leneta测试卡上。然后使浇铸的膜在室温下干燥1个小时，之后在50℃下使涂层老化16个小时。使涂层在1小时内冷却至室温。

[0175] 然后，评估经涂布的卡片对如下污物的耐污性：水、乙醇（48％）、洗涤剂（Andy，50％溶液）、咖啡、热锅。在所有情况下，在涂层上放置各个污物的斑点（1cm^2），并用一片滤纸和表面皿将其覆盖。在“热锅测试”的情况下，在测试卡上将充满沸腾热水的小玻璃烧杯放置在冷水上。将所有提到的斑点静置一小时；还测试16小时的水、乙醇（48％）和洗涤剂（50％）。这些时间段后，用纸巾轻轻擦去斑点，并且评估膜的完整性。将其在0和5之间评级，其中0＝膜完全破损／强烈变色并且5＝膜完好无损且没有任何缺陷／变色。涂层的结果明确示于下表2A和2B中。

[0176] 表2A：性质

[0177]

实例	硬度	耐性 1h				
		W	E48%	A50%	C	HP
A	36	1	0	1	2	0
1	121	5	4	5	4	5
B	68	2	1	2	2	2
2	85	5	4-5	5	4-5	4
3	87	5	4	5	4-5	4-5
4	102	5	3-4	5	5	2
5	113	5	2	5	5	4-5

[0178] 表2B：性质（继续）

[0179]

实例	耐性 16h				总评分
	W	E48%	A50%	C	
A	0	0	1	1	6
1	5	0-1	4-5	2	35
B	2	0-1	3	1	15.5
2	5	4	5	3-4	40.5
3	5	5	5	2	40
4	5	3	4-5	5	38
5	5	1	4-5	4-5	36.5

[0180] 硬度＝König硬度（秒）

[0181] W＝水

[0182] E48％＝乙醇，在去矿物质中的48％溶液

[0183] A50％＝Andy，在去矿物质中的50％溶液（洗涤剂）

[0184] C＝咖啡

[0185] HP＝热锅

[0186] 总评分＝在耐污性方面所有单个分数的总和

Abstract

There is described a process for preparing a Schiff base crosslinkable aqueous dispersion of a polyurethane A (PUD) the process comprising(a) reacting components (1) to (4) as present to form an acidic isocyanate terminated prepolymer that comprises anionic or potentially anionic functional groups thereon; where: (1) component one comprises 10 to 80% by weight of at least one polyisocyanate optionally containing at least one anionic or potentially anionic dispersing group; (2) optional component two comprises up to 15% by weight of at least one isocyanate-reactive polyol containing at least one anionic or potentially anionic dispersing group; (3) component three comprises 15 to 85% by weight of at least one isocyanate reactive polyol other than component two if present, and having a weight average molecular weight greater than or equal to 500 Daltons optionally containing at least one anionic or potentially anionic dispersing group; and (4) optional component four comprises up to 20% by weight of at least one isocyanate reactive polyol other than component three and two if present and having a weight average molecular weight less than 500 Daltons; where if component two is not present component one or three contains at least one anionic or potentially anionic dispersing group; where the amounts of components one to four are expressed as a weight percentage calculated from the total amount of the above components (i.e. one and three and optional two and/or four where present) being 100%; and where the mixture used in step (a) is substantially free of volatile amines and N-alkyl pyrrolidinones; (b) adding to the reaction mixture from step (a) an alkali metal neutralising agent in an amount from 0.05 to 6 parts by weight substantially to neutralise the isocyanate terminated prepolymer obtained from step (a); where the amount (in weight parts) of the alkali metal neutralising agent is calculated based on the weight of alkali metal in the neutralising agent relative to the total amount of components one to four in step (a) being equal to 100 parts; and (c) reacting the neutralised prepolymer from step (b) with an active hydrogen compound to extend the chain of the prepolymer to form an aqueous dispersion of polyurethane A. and (ii) 90 to 5% by weight of a vinyl polymer B wherein the weight % amounts of (i) and (ii) are calculated as a percentage of the total amount of (i) and (ii) and these percentages add up to 100%; and where the composition is: substantially free of volatile amines and N-alkyl pyrrolidinones (preferably solvent free); and is neutralised with a metal neutralising agent and the composition comprises a polyamine of polyhydrazide compound. Another aspect of the invention provides an aqueous coating obtained from the above process, in which polyurethane A and/or vinyl polymer B is Schiff base cross-linkable under ambient conditions.