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Aqueous Resin Dispersions

Abstract

Aqueous resin dispersions obtainable by reaction or partial reaction, of hydroxy-containing ketone, ketone/aldehyde and/or urea/aldehyde resins or hydrogenated follow-on products thereof and at least one hydrophilically modified isocyanate and/or polyisocyanate having at least one free NCO group, obtainable by reacting at least one isocyanate and/or polyisocyanate with compounds which in addition to the hydrophilic or potentially hydrophilic group have at least one isocyanate-reactive function and which possess a hydrogen which is active according to the Zerewitinoff test, and which also possess at least one hydrophilic group and/or one potentially hydrophilic group, and then combining the neutralised resin with water.

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Invention Title: Aqueous Resin Dispersions

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

Aqueous Resin dispersions

The present invention relates to aqueous ketone, ketone/aldehyde or urea/aldehyde resin dispersions, to a process for their preparation and to their use.

The condensation of ketone, ketone/aldehyde and urea/aldehyde resins is known (Ullmann's Encyclopedia of Industrial Chemistry, VCH Verlagsgesellschaft mbH Weinheim 1993, Vol. 23, pp. 99-105). Such resins are generally insoluble in water.

DE-A 25 42 090 describes water-soluble compounds which carry sulfonic acid groups and which, in deviation from the novel process, are obtainable in a conjoint condensation reaction from cycloalkanone, formaldehyde and alkali metal bisulfite.

DE-A 31 44 673 indicates water-soluble condensation products which are likewise obtained by conjoint reaction of ketones, aldehydes and compounds which introduce acid groups. Examples of the latter are sulfites and salts of amidosulfonic acid, of aminoacetic acid and of phosphorous acid.

According to DE-A 25 42 090 and DE-A 31 44 673, the products obtained include electrolyte (eg. Na ions). However, such resins impair, inter alia, the corrosion protection afforded by coating systems.

DE-A 34 06 473 and DE-A 34 06 474, or EP-A 0 154 835, describe processes for preparing stable aqueous dispersions of urea/aldehyde resins or, respectively, ketone/(aldehyde) resins, in accordance with which the resin melt or a highly concentrated solution thereof is dispersed in water in the presence of organic protective colloids and with or without the addition of emulsifiers. A disadvantage of this process is that the organic protective colloids and emulsifiers interfere with the use of the aqueous ketone/(aldehyde) and urea/aldehyde resins in the coating sector. The hydrophilic protective colloids and, if used, emulsifiers remain in the coating and thus make it sensitive to moisture. The coating swells under the action of moisture, loses hardness and suffers a loss of some of its corrosion protection effect.

The object of the invention was to develop ketone, ketone/aldehyde or urea/aldehyde resin dispersions and a process for their preparation. The resin dispersions are to be stable to hydrolysis and stable on storage and should not have the disadvantages described above. At the same time, the properties customary for such resins should be retained.

The object on which the invention is based is achieved by reacting hydroxy containing ketone, ketone/aldehyde, and/or urea/aldehyde resins or hydrogenated follow-on products thereof with hydrophilically modified (poly)isocyanates.

Following neutralisation and the addition of water, the novel ketone, ketone/aldehyde and/or urea/aldehyde resins modified in this way give rise to stable aqueous solutions, dilutions and dispersions.

In comparison with the systems already known from the prior art the novel aqueous systems are completely stable to hydrolysis and include no interfering additives whatsoever in the form, for example, of emulsifiers, protective colloids or electrolytes.

The present invention provides aqueous resin dispersions obtained by reaction, or partial reaction of hydroxy-containing ketone, ketone/aldehyde and/or urea/aldehyde resins or hydrogenated follow-on products thereof and at least one hydrophilically modified isocyanate and/or polyisocyanate having at least one free NCO group, obtainable by reacting at least one isocyanate and/or polyisocyanate with compounds which in addition to the hydrophilic or potentially hydrophilic group have at least one isocyanate-reactive function and which possess a hydrogen which is active according to the Zerewitinoff test, and which also possess at least one hydrophilic group and/or one potentially hydrophilic group, and then combining the neutralised resin with water.

The hydrophilic modification of II is effected by reacting a (poly)isocyanate and/or mixtures of different (poly)isocyanates with compounds having (in addition to the hydrophilic or potentially hydrophilic group) at least one isocyanate-reactive function, for example OH, NH, which has a hydrogen which is active according to the Zerewitinoff test, and having at least one hydrophilic group and/or one potentially hydrophilic group, ie. a group which becomes hydrophilic after neutralisation. Examples of such compounds for hydrophilic modification of the polyisocyanates are aminocarboxylic acids, hydroxysulfonic acids, aminosulfonic acids and also hydroxycarboxylic acids, such as, with particular preference, dimethylolpropionic acid.

The hydrophilic modification can also be undertaken with already neutralised compounds.

Hydroxycarboxylic acids such as, in particular, dimethylolpropionic acid are particularly preferred because when neutralised with volatile bases, for example amines, they exhibit a strong hydrophilic effect which, however, recedes sharply when the volatile base evaporates, with the result, for example, that coatings do not soften or whiten under the effect of moisture.

Dimethylolpropionic acid is also particularly preferred because by way of its two hydroxy groups it has the capacity to provide two hydrophobic polyisocyanates with (potentially) hydrophilic modification.

Suitable polyisocyanates for preparing II are, preferably, di- to tetrafunctional polyisocyanates having a molar mass of below 800g/mol and having isocyanate groups attached to aliphatic, (cyclo)aliphatic and/or cycloaliphatic structures, as are commonly employed in the field of polyurethane coating materials, and also mixtures of these polyisocyanates: 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate, IPDI), trimethylhexamethylene diisocyanate (TMDI), 1,6-diisocyanatohexane (HDI), bis(4-isocyanatohexyl)methane (H_{12}MDI), and also other polyisocyanates, which are listed in DE-A 24 56 469, pp. 5 and 6.

Less preferred, but suitable for the invention, are oligomers which are obtainable from the monomeric polyisocyanates in accordance with the prior art, as described, for example, in Journal für Praktische Chemie 336 (1994), 185-200 and Farbe und Lack 100, 5 (1994), 330-335 and the literature indicated therein. These are polyisocyanates having a biuret, uretdione or isocyanurate structure, the latter obtainable by cyclotrimerisation of the monomers. Also suitable, moreover, are polyisocyanates as products of polyhydric alcohols and/or of amines with monomeric isocyanates, for example the product of trimethylolpropane and isophorone diisocyanate.

Particular preference is given to a hydrophilically modified polyisocyanate II prepared from dimethylolpropionic acid and isophorone diisocyanate (IPDI) in a molar ratio of 1:2.

The reaction of I and II can be carried out without solvent or, preferably, in the presence of an auxiliary solvent. When an auxiliary solvent is used, preferred solids contents are from 50 to 95% by mass, particularly preferably from 60 to 80% by mass.

Suitable auxiliary solvents are either, preferably, those which have a boiling point of below 100°C at 1013hPa and which can be separated off in full again from the finished aqueous system, down to a residual content of <0.5% by mass, and re-used, for example acetone. methyl ethyl ketone or tetrahydrofuran, or, less preferably, those which may be higher-boiling and which remain in the water-dilutable system, for example butylglycol, butyl diglycol or N-methylpyrrolidone. The auxiliary solvents which boil below 100°C are preferred because they make it possible to prepare purely aqueous, solvent-free and thus particularly environmentally compatible dispersions. The use of the higher-boiling solvents - in whole or in part - or solvent mixtures with a boiling point above 100°C, although technically possible, is not preferred and is not aimed at. An advantage of the novel process, indeed, is that it is possible to do entirely without organic solvents in the finished aqueous resin dispersion and nevertheless to obtain high-solids stable dispersions.

The reaction of I and II is preferably allowed to proceed to such an extent that the residual NCO content is less than 1% NCO (determined in accordance with DIN 53185) and with particular preference is allowed to proceed to an extent such that the residual NCO content of the product of I and II is in the range from 0.1 to 0.5% NCO. NCO functions which remain unreacted in the reaction of I and II can, in accordance with the prior art, either be used for chain extension reactions, for example by addition of polyamines or water, or, if desired, chain termination can be initiated by adding compounds which are monofunctional with respect to NCO groups (eg. monoalcohols, monoamines).

The resins prepared in accordance with the invention can be neutralised with inorganic and organic bases, for example ammonia or organic amines. It is preferred to use primary, secondary and tertiary amines, for example ethylamine, propylamine, dimethylamine, dibutylamine, cyclohexylamine, benzylamine, morpholine, piperidine and triethanolamine. Particular preference is given to volatile tertiary amines, especially dimethylethanolamine, diethylethanolamine, 2-dimethylamino-2-methyl-1-propanol, triethylamine, tripropylamine and tributylamine.

The amount of neutralising agent depends on the content of potentially neutralisable groups in the hydrophillically modified polyisocyanate and is preferably from 50 to 130% of the amount necessary for stoichiometric neutralisation.

The neutralised hydrophilic resin or the resin solution is either passed into water or has water added to it, preferably with stirring. Prior to the addition of water it is possible to combine the reaction product of I and II with, if desired, further resins, which have not been hydrophilically adjusted, or with other components, and then to disperse these combinations together. By this means it is possible to obtain an industrially advantageous, high solids content of the dispersions, of more than 45% by mass.

Following dispersion, the organic auxiliary solvent is preferably removed *in vacuo* and, if desired, is reprocessed.

The novel resin dispersions possess good storage stabilities and are suitable as resins or additional resins in coating materials such as paints and printing inks, for example. They are also suitable for aqueous ballpoint pen pastes and inks. Such resin dispersions are also suitable for use in adhesives, for example for the bonding of textiles, leather, paper and similar materials.

The dispersions show good wetting properties, even in combination with difficult organic pigments, and can therefore be used as a gloss-promoting additional resin in paste binders.

Owing to the usually very high softening point combined with good solubility and compatibility, the resulting coatings show rapid initial drying and through-drying, and good blocking resistance.

Example

The invention is illustrated using the following example.

1) Preparing the hydrophilically modified polyisocyanate II and reacting it with I

444g of isophorone diisocyanate are added with stirring to a mixture of 134g of dimethylolpropionic acid (DMPA), 380g of acetone and 6g of a 10% strength by mass solution of dibutyltin dilaurate (DBTL) in acetone at a rate such that the exothermic reaction remains readily manageable. The mixture is then stirred further at 60°C until the DMPA has completely dissolved and the NCO number of the solution has fallen below 8.7% NCO (determined in accordance with DIN 53185).

The solution is cooled to room temperature, 2300g of a 55% strength by mass solution in acetone of an acetophenone/formaldehyde resin subsequently hydrogenated in respect of the keto function (Kunstharz [synthetic resin] SK from Hüls AG) and 12g of a 10% strength by mass solution of DBTL in acetone are added, and the mixture is heated to the reflux temperature of about 60°C. Stirring is continued at this temperature until the NCO number of the solution has fallen below 0.3% NCO.

2) Dispersing the hydrophilically modified resin obtained from I and II

Alternative A:

The solution of the hydrophilically modified resin as prepared under 1) is neutralised at room temperature, with stirring, by addition of 89g of dimethylaminoethanol and the solution is dispersed by introducing 4200g of fully deionised water, again with stirring. The auxiliary solvent, acetone, and some of the water are removed *in vacuo* to give a storage-stable, fine, slightly opalescent resin dispersion having a solids content of about 33% by mass.

Alternative B:

To the solution prepared under 1) there are added, with stirring, 3300g of a 55% strength by mass solution, in acetone, of an acetophenone/formaldehyde resin subsequently hydrogenated with respect to the keto group (Kunstharz 5K from Hüls AG), the mixture is neutralised at room temperature and with stirring using 89g of dimethylaminoethanol, and the solution is dispersed by introducing 4400g of fully deionised water, again with stirring. The auxiliary solvent, acetone, and some of the water are removed *in vacuo* to give a storage-stable, whitish dispersion having a solids content of about 50% by mass.

3) Properties of the dispersion and pigment pastes prepared therefrom

Storage stability

The dispersions A and B of Section 2) were investigated for storage stability in respect of changes in pH, in viscosity and in visual appearance.

Property	A	B
pH: Initial value	8.9	8.8
pH: After ½ year	8.9	8.8
Viscosity 23°C**: Initial value	375 - 714 mPa.s	69 -138 mPa.s
Viscosity 23°C**: After ½ year	335 - 563 mPa.s	67 -135 mPa.s
Appearance: After preparation	Slightly opalescent	White
Appearance: After ½ year	Slightly opalescent	White

** Rotary viscometer; D: 100 to 900 s^{-1}

Testing the pigment wetting

White pigment concentrates were prepared in the customary manner using the dispersions A and B of Section 2).

	Amounts in Parts by Weight	
Constituent	A	B
KRONOS 2190®	63.0	63.0
Dispersion	16.3	10.8
DISPERBYK 181®	2.0	2.0
DISPERBYK 184®	4.8	4.8
BYK-022®	0.5	0.5
Aerosil 200®	0.3	0.3
Water (demin.)	13.1	18.6
Pigment concentrate	100.0	100.0

The pigment concentrates had good rheological properties and good flocculation stability.

The pigment concentrates were made up to the coating material by adding 20 parts by weight of pigment concentrate to the alkyd/melamine resin coating base system indicated below. In this context it was possible to mix in the pigment concentrates without problems.

Alkyd/melamine resin system

WORLEESOL 61 A®	47.8 parts by weight
CYMEL 327®	8.6 parts by weight
Butylglycol	3.9 parts by weight
Dimethylethanolamine	2.4 parts by weight
BYK 301®	0.2 part by weight
Water (demin.)	37.1 parts by weight
Coating base binder	100.0 parts by weight

Paint films on steel plate were prepared and evaluated in the customary manner.

Paint film properties

Property tested	A	B
Gloss 60°	93	98
Pendulum hardness(König) D1N53157	120s	106s
Indentation (Erichsen) DIN 53156	7.5 mm	8.5 mm
Adhesion (crosshatch) DIN 53151	0	0

The claims defining the invention are as follows:

1. An aqueous resin dispersion obtained by reaction, or partial reaction, of

I. hydroxy-containing ketone, ketone/aldehyde and/or urea/aldehyde resins or hydrogenated follow-on products thereof and

II. at least one hydrophilically modified isocyanate and/or polyisocyanate having at least one free NCO group, obtainable by reacting at least one isocyanate and/or polyisocyanate with compounds which in addition to the hydrophilic or potentially hydrophilic group have at least one isocyanate-reactive function and which possess a hydrogen which is active according to the Zerewitinoff test, and which also possess at least one hydrophilic group and/or one potentially hydrophilic group, and then combining the neutralised resin with water.

2. The resin dispersion as claimed in claim 1, wherein component II is prepared using tertiary amino alcohols, aminocarboxylic acids, hydroxysulfonic acids, aminosulfonic acids and/or hydroxycarboxylic acids.

3. The resin dispersion as claimed in claim 1, wherein component II is prepared using dimethylolpropionic acid.

4. The resin dispersion as claimed in any one of claims 1 to 3, wherein component II is already neutralised before reaction with component I.

5. The resin dispersion as claimed in any one of claims 1 to 4. wherein II is prepared using di- to tetrafunctional polyisocyanates having a molar mass of below 800g/mol.

6. The resin dispersion as claimed in any one of claims 1 to 5, wherein II is prepared using polyisocyanates having isocyanate groups attached to aromatic, aliphatic and/or cycloaliphatic structures, or mixtures thereof.

7. The resin dispersion as claimed in any one of claims 1 to 6, wherein 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate, IPDI), trimethylhexamethylene diisocyanate (TMDI), 1,6-diisocyanatohexane (HDI) or bis(4-isocyanatohexyl)methane (H_{12}MDI) are employed.

8. The resin dispersion as claimed in any one of claims 1 to 7, wherein II is prepared using polyisocyanates having a biuret, uretdione or isocyanurate structure.

9. The resin dispersion as claimed in any one of claims 1 to 8, wherein II is prepared using polyisocyanates from the reaction of polyhydric alcohols and/or of amines with monomeric isocyanates.

10. The resin dispersion as claimed in any one of claims 1 to 7, wherein II is prepared using dimethylolpropionic acid and isophorone diisocyanate (IPDI) in a molar ratio of 1: 2.

11. The resin dispersion as claimed in any one of claims 1 to 10, wherein the reaction of I and II and the dispersion can be carried out without solvent.

12. The resin dispersion as claimed in any one of claims 1 to 10, wherein the reaction of I and II and the dispersion can take place in the presence of an auxiliary solvent.

13. The resin dispersion as claimed in any one of claims 1 to 12, wherein the auxiliary solvent used has a boiling point of below 100°C at 1013hPa.

14. The resin dispersion as claimed in any one of claims 1 to 13, wherein the auxiliary solvent used is acetone and/or methyl ethyl ketone and/or tetrahydrofuran.

15. The resin dispersion as claimed in any one of claims 1 to 14, wherein neutralisation is carried out with inorganic or organic bases.

16. The resin dispersion as claimed in any one of claims 1 to 15, wherein dimethylethanolamine and/or diethylethanolamine and/or 2-dimethylamino-2-methyl-1-propanol are used for neutralisation.

17. The resin dispersion as claimed in any one of claims 1 to 16, wherein neutralisation is carried out using from 50 to 130% of the amount of neutralising agent required for stoichiometric neutralisation.

18. The resin dispersion as claimed in any one of claims 1 to 17, wherein prior to addition of water one or more components are added which are not soluble in water or dilutable in water.

19. An aqueous resin dispersion, substantially as hereinbefore described with reference to the example.

20. A resin or additional resin in coating materials containing the resin dispersion as claimed in any one of claims 1 to 19.

21. A resin or additional resin in ballpoint pen pastes and inks containing the resin dispersion as claimed in any one of claims 1 to 19.

22. A resin or additional resin in adhesives containing the resin dispersion as claimed in any one of claims 1 to 19.

23. A resin or additional resin in pigment pastes containing the resin dispersion as claimed in any one of claims 1 to 19.

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