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(54) Title: TWO-COMPONENT POLYURETHANE BINDERS AS ADHESION PROMOTERS

(57) **Abrégé/Abstract:**

The invention relates to the use of polyurethane bonding agents as adhesives, said bonding agents having two constituents and containing a solvent. Said bonding agents also contain a hardening constituent consisting of an addition product of a polyisocyanate with an alkoxy silane and a resin for lacquers and varnishes which reacts in relation to isocyanate groups.



Abstract

The invention relates to the use of polyurethane bonding agents as adhesives, said bonding agents having two constituents and containing a solvent. Said bonding agents also contain a hardening constituent consisting of an addition product of a polyisocyanate with an alkoxy silane and a resin for lacquers and varnishes which reacts in relation to isocyanate groups.

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Two-component polyurethane binders as adhesion promoters

5 The invention relates to the use of solventborne two-component polyurethane binders as adhesion promoters which are applied to a substrate and to which subsequently an organic or inorganic coating or an organic-inorganic hydride coating is applied.

10 Plastics are extremely diverse materials having a range of desirable properties. A disadvantage of these materials, however, is, for example, their sensitivity to mechanical damage on the surface or to chemicals, such as solvents.

One method of protecting the surface of plastics against such damage consists in applying to the plastics substrate a suitable coating. The composition of the coating is primarily dependent on whether the surface is to be protected more against
15 mechanical damage, radiation, the action of chemicals, or other environmental effects (e.g., soiling, etc.). Transparent plastics, such as polycarbonate, are particularly sensitive to superficial mechanical damage. Consequently, numerous coating materials are known which provide effective protection against mechanical damage to polycarbonates in particular. These are essentially organically modified
20 inorganic coatings, which are usually condensation- or UV-curing. Examples can be found in J. Sol-Gel Sci. Techn. 1998, 11, 153-159, Abstr. 23rd, Annual Conference in Organic coatings, 1997, 271-279, EP-A 0 263 428, DE-A 29 14 427 and DE-A 43 38 361.

25 The application of these inorganic coatings, however, is often attended by the problem that the adhesion between plastic and coating is inadequate. In order to obtain sufficient adhesion in spite of this, a series of methods has already been described in the prior art. Physical methods include, for example, plasma treatment or corona treatment; an example of a suitable chemical method is the use of an
30 adhesion promoter (primer).

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Many adhesion promoters react both with the plastic surface and with the coating, and (covalent) chemical bonds are formed. In the case of polycarbonate substrates use is made, for example, of aminosilanes, such as aminopropyltrialkoxysilanes (e.g. in DE-A 19 858 998). In this case the amino group reacts with the polycarbonate surface, and the alkoxysilyl radicals with the organically modified, silicon-containing inorganic coating. These N-H functional adhesion promoters have the disadvantage, however, that the polycarbonate suffers considerable damage as a result of the basic nitrogen function, this being manifested, for example, visually in a distinct yellowing. A further disadvantage is that the adhesion of the inorganic/organic hybrid coatings is rapidly reduced on deployment in water, especially warm water. The film, for example, becomes cloudy, blistering occurs, and ultimately the film is delaminated completely.

The present invention provides an adhesion promoter (primer) for silicon-containing coatings on polymeric substrates which permits good adhesion between the organically modified, silicon-containing inorganic coating and the surface of the polymeric substrate and which leads neither to optical damage nor to a lability toward water.

It has now been found that solventborne two-component polyurethane binders which comprise a curing component composed of an adduct of a polyisocyanate with an alkoxysilane and a film-forming resin reactive toward isocyanate groups can be used as adhesion promoters. These solventborne 2-K systems constitute an ideal combination of very high promotion of adhesion between, for example, polymeric substrate and inorganic coating and a very good weathering stability.

Adducts of, for example, polyisocyanates with aminosilanes are already state of the art. Moisture-curing, alkoxysilane-terminated polyurethanes of this kind are used in flexible, room temperature-curing sealants and adhesives (e.g., US-A 5 700 868, US-A 4 625 012, US-A 4 474 933, US-A 3 979 344, DE-A 4 234 325, DE-A 2 155 259).

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Furthermore, H. Ni et al. in "Polymer 41 (2000), pp. 57-71" describe the use of a reaction product of HDI-isocyanurate with 3-aminopropyltriethoxysilane as an improved coating system for aircraft.

5 US-A 5 854 338 discloses a binder combination for water-thinnable two-component polyurethane coatings, which is composed of an aqueous hydroxy- and/or amino-functional acrylate dispersion and a curing component containing isocyanate groups and alkoxysilyl groups in a certain ratio. The alkoxysilyl groups are prepared by a reaction of a nonmodified polyisocyanate with corresponding amino-functional
10 alkoxysilyl compounds. The incorporation of the alkoxysilyl compounds into the curing component makes it possible to obtain two-component polyurethane coatings having an improved profile of properties in respect of hardness, acid resistance or adhesion.

15 The present inventions provide for the use of solventborne two-component polyurethane binders comprising

1. a curing component (A) comprising an adduct of
20 at least one organic polyisocyanate (B) having an average NCO functionality of from 2.5 to 5.0 and an isocyanate content of from 8 to 27% by weight and an alkoxysilane (C) having at least one isocyanate-reactive group of the general formula (I)



in which

30 Q is an isocyanate-reactive group, preferably OH, SH or NHR_1 , where R_1 is a C_1 - C_{12} alkyl group or C_6 - C_{20} aryl group or is $-Z-SiX_aY_{3-a}$,

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Z is a linear or branched C₁-C₁₂ alkylene group, preferably a linear or branched C₁-C₄ alkylene group,

X is a hydrolyzable group, preferably C₁-C₄ alkoxy,

5

Y is identical or different C₁-C₄ alkyl groups, and

a is an integer from 1 to 3,

10 and

2. an isocyanate-reactive film-forming resin (D),

as adhesion promoters.

15

The ratio of the isocyanate-reactive groups of the film-forming resin (D) to the isocyanate groups of the curing agent (A) lies between 0.5 : 1 to 2 : 1, preferably between 0.7 : 1 to 1.3 : 1.

20 The polyisocyanate (B) containing in the curing component (A) preferably has an average NCO functionality of from 2.3 to 4.5 and preferably has an isocyanate group content of from 11.0 to 24.0% by weight. The monomeric diisocyanate content is less than 1% by weight, preferably less than 0.5% by weight.

25 The polyisocyanate (B) is composed of at least one organic polyisocyanate having aliphatically, cycloaliphatically, araliphatically and/or aromatically attached isocyanate groups.

30 The polyisocyanates or polyisocyanate mixtures (B) comprise any desired polyisocyanates which are prepared by modification of simple aliphatic, cycloaliphatic, araliphatic and/or aromatic diisocyanates, are synthesized from at least two diisocyanates, and have a uretdione, isocyanurate, allophanate, biuret,

iminooxadiazinedione and/or oxadiazinetriene structure, such as are described exemplarily in, for example, *J. Prakt. Chem.* 336 (1994) 185 – 200 and in DE-A 16 70 666, DE-A 19 54 093, DE-A 24 14 413, DE-A 24 52 532, DE-A 26 41 380, DE-A 37 00 209, DE-A 39 00 053 and DE-A 39 28 503 or in EP-A 336 205, EP-A 339 396, and EP-A 798 299.

Suitable diisocyanates for preparing such polyisocyanates are any desired diisocyanates which are obtainable by phosgenation or by phosgene-free methods, by thermal urethane cleavage for example, are of the molecular weight range 140 to 400, and have aliphatically, cycloaliphatically, araliphatically and/or aromatically attached isocyanate groups, such as, for example, 1,4-diisocyanatobutane, 1,6-diisocyanatohexane (HDI), 2-methyl-1,5-diisocyanatopentane, 1,5-diisocyanato-2,2-dimethylpentane, 2,2,4- and/or 2,4,4-trimethyl-1,6-diisocyanatohexane, 1,10-diisocyanatodecane, 1,3- and 1,4-diisocyanatocyclohexane, 1,3- and 1,4-bis(isocyanatomethyl)cyclohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate, IPDI), 4,4'-diisocyanatodicyclohexylmethane, 1-isocyanato-1-methyl-4(3)isocyanatomethylcyclohexane, bis(isocyanatomethyl)norbornane, 1,3- and 1,4-bis(1-isocyanato-1-methylethyl)benzene (TMXDI), 2,4- and 2,6-diisocyanatotoluene (TDI), 2,4'- and 4,4'-diisocyanatodiphenylmethane (MDI), 1,5-diisocyanatonaphthalene or any desired mixtures of such diisocyanates.

The starting components (B) are preferably polyisocyanates or polyisocyanate mixtures of the stated kind having exclusively aliphatically and/or cycloaliphatically attached isocyanate groups.

Especially preferred starting components (B) are polyisocyanates or polyisocyanate mixtures with biuret or isocyanurate structure based on HDI, IPDI and/or 4,4'-diisocyanatodicyclohexylmethane.

Suitable alkoxysilanes (C) having isocyanate-reactive functional groups of the general formula (I) are, for example, hydroxymethyltri(m)ethoxysilane and

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alkoxysilyl compounds having secondary amino groups or mercapto groups. Examples of secondary aminoalkoxysilanes are N-methyl-3-amino-propyltri(m)ethoxysilane, N-phenyl-3-aminopropyltrimethoxysilane, bis(gamma-trimethoxysilylpropyl)amine, N-butyl-3-aminopropyltri(m)ethoxysilane, N-ethyl-3-
 5 aminoisobutyltri(m)ethoxysilane or N-ethyl-3-aminoisobutylmethyldi(m)ethoxy-silane, and also the analogous C₂-C₄ alkoxysilanes.

Alkoxysilanes (C) likewise suitable in the sense of the invention are amino-functional alkoxysilyl compounds obtained in accordance with the teaching of US-A
 10 5 364 955 by the reaction of aminosilanes of the aforementioned general formula (I) in which R₁ = H with maleic or fumaric esters of the general formula (II)



15 in which

R₂ and R₃ are identical or different (cyclo)alkyl radicals having 1 to 8 carbon atoms.

20 Preferred compounds of the general formula (II) are dimethyl maleate and diethyl maleate.

Further examples of alkoxysilanes (C) having an isocyanate-reactive functional group of the general formula (I) are 3-mercaptopropyltrimethoxysilane and
 25 3-mercaptopropyltriethoxysilane.

Preferred alkoxysilanes (C) are N-butyl-3-aminopropyltri(m)ethoxysilane and 3-mercaptopropyltri(m)ethoxysilane.

To prepare the curing agent (A) employed in the use according to the invention it is
 30 of course also possible to use mixtures of said alkoxysilanes (C) of the general formula (I). Possible by way of example are mixtures of alkoxysilanes (C) which contain the same isocyanate-reactive functional group Q but different hydrolyzable

groups X. Also suitable are mixtures comprising alkoxysilanes (C) of the general formula (I) with different functional groups Q.

The modification of the polyisocyanate components (B) with alkoxysilanes (C) takes place in a molar NCO/Q ratio of 1 : 0.01 to 0.75, preferably in a molar NCO/Q ratio of 1 : 0.05 to 0.4, Q having the meaning indicated in the general formula (I).

In principle it is naturally also possible to react polyisocyanates with the amino-functional alkoxsilyl compounds ($Q = NH$) employed in the inventive use in a higher molar ratio or even completely, i.e., corresponding to an NCO/Q ratio of 1 : 1.

Suitable isocyanate-reactive film-forming resins (D) are polyhydroxyl compounds, such as, for example, tri- and/or tetrafunctional alcohols and/or the customary polyetherpolyols, polyesterpolyols, polycarbonatepolyols and/or polyacrylatepolyols.

Also suitable in principle as reaction partners (D) for the curing agent (A) employed in the use according to the invention are film-forming binders or film-forming binder components having isocyanate-reactive groups other than hydroxyl groups. These include, for example, polyurethanes or polyureas, which can be crosslinked with polyisocyanates owing to the active hydrogen atoms present in the urethane or urea groups, respectively. Examples of further suitable reaction partners (D) include polyamines whose amino groups have been blocked, such as polyketimines, polyaldimines or oxazolanones, for example, from which, under the influence of moisture, free amino groups and, in the case of the oxazolanones, free hydroxyl groups are formed, which are able to react with the polyisocyanate mixtures. Preferred film-forming resins (D) are polyacrylatepolyols and polyesterpolyols.

In the solventborne 2-K PU binder used according to the invention the polyisocyanate components and/or binder components are generally employed in a form in which they are diluted with solvents. These solvents are, for example, butyl acetate, ethyl acetate, 1-methoxy-2-propyl acetate, toluene, 2-butanone, xylene, 1,4-dioxane, diacetone alcohol, N-methylpyrrolidone, dimethylacetamide,

dimethylformamide, dimethyl sulfoxide or any desired mixtures of such solvents. Preferred solvents are butyl acetate, ethyl acetate and diacetoalcohol.

5 As further components it is possible if desired to add the auxiliaries customary in coatings technology to the solvent-containing 2-K PU binders used according to the invention. Customary auxiliaries are all additives known for the preparation of varnishes and paints, such as organic or inorganic pigments, light stabilizers, coatings additives, such as dispersants, leveling agents, thickeners, defoamers and other assistants, tackifiers, fungicides, bactericides, stabilizers or inhibitors, and
10 catalysts. It is of course also possible to add two or more of said auxiliaries.

The 2-K PU binder used according to the invention is applied to a substrate by the application methods which are customary in coating technology, such as spraying, flow coating, dipping, spin coating or knife coating, for example.

15

Examples of suitable substrates in accordance with the invention include polymeric substrates, such as ABS, polyamide or polyurethane, for example, metals, which may where appropriate have an organic coating, or else glass.

20 The 2-K PU binder used as adhesion promoter in accordance with the invention is particularly suitable for transparent polymeric substrates, for example, for thermoplastic polymers, such as polycarbonates, polymethyl methacrylates, polystyrene, polyvinylcyclohexane and its copolymers or polyvinyl chloride or blends thereof.

25

To the substrates coated with the adhesion promoter used in accordance with the invention it is possible to apply inorganic coatings, such as, for example, purely inorganic coating systems or else organically modified inorganic coating systems or else coats deposited by way of a plasma process (e.g., Al_2O_3 , TiO_2 , SiO_x , TiC etc.).

30

By purely inorganic coating systems are meant, for example, those coatings produced by the sol-gel process which are composed of monomer units which carry no organic

groups which if present, and given an ideal network structure, might remain as constituents in the network.

5 Examples of monomer units of this kind are tetraalkoxysilanes, such as tetra(m)-ethoxysilane, or else metal alkoxides such as aluminum, titanium or zirconium alkoxide.

Furthermore, such inorganic coating systems may of course also include inorganic filler particles, such as SiO_2 , Al_2O_3 or AlOOH .

10

By organically modified inorganic coating systems are meant, for example, those coatings produced by way of the sol-gel process which are composed of monomer units which carry organic groups which remain as constituents in the network that forms. These organic groups may be functional or nonfunctional.

15

Monomer units with nonfunctional organic groups include, for example, alkylalkoxysilanes, such as methyltri(m)ethoxysilane, arylalkoxysilanes or phenyltri(m)ethoxysilane, and also carbosilane compounds, as described, for example, in US-A 5 679 755, US-A 5 677 410, US-A 6 005 131, US-A 5 880 305 or
20 in EP-A 947 520.

Monomer units with functional organic groups include, for example, alkoxysilanes containing vinyl, acryloyl or else methacryloyl groups, such as vinyltri(m)ethoxysilane, acryloyloxypropyltri(m)ethoxysilane or methacryloyloxypropyltri(m)ethoxy-
25 silane, and epoxy-functional alkoxysilanes, such as glycidyloxypropyltri(m)ethoxysilane, or else NCO-functional alkoxysilanes, such as 3-isocyanatopropyltri(m)ethoxysilane.

30 With monomer units of this kind it is possible among other things to construct a crosslinking organic polymer system alongside the inorganic network which exists or is formed.

Functional organic groups should also be understood, however, to include those which do not necessarily serve for the construction of an organic crosslink, examples being halogens, acid groups, alcohol or thiol groups. Examples of suitable organic coatings are polyurethane systems, melamine resin crosslinking systems or else alkyd
5 resin coating systems.

Preferred in addition to the inorganic coatings are also organic-inorganic hybrid coatings. These have the feature that they possess not only an organic polymer system but also an inorganic polymer system, which are present alongside one
10 another or linked.

Possible organic-inorganic hybrid coatings are, for example, those in which an organic polymer matrix has been modified by the addition or incorporation of inorganic structural units. Inorganic structural units can be, for example, silica sol
15 dispersions in water or in organic solvents and/or hydrolyzates of (organic-functional) alkoxysilanes.

Particularly high abrasion resistance and scratch resistance and also a very good solvent resistance are achieved if a coating system based on organo-functional
20 alkoxysilanes and/or siloxanes is applied to the polymeric substrate coated with the adhesion promoter used in accordance with the invention. A widely known process for preparing such film-forming binders is the sol-gel process as described exhaustively by C.J. Brinker and W. Scherer in "Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing, Academic Press, New York (1990). Suitable sol-
25 gel coating materials of high mechanical stability are state of the art and are described for example in US-A 4 624 870, US-A 3 986 997, US-A 4 027 073, EP-A 358 011, US-A 4 324 712, WO 98/52992, WO 94/06 807, US-A 6 005 131, and EP-A 947 520. Hydrophobic and/or oleophobic organic-inorganic hybrid coatings having antistick and/or antigraffiti properties are described for example in DE-A 41
30 18 184, WO 99 03 941, and EP-A 967 253.

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Polymeric substrates can therefore be effectively protected against mechanical damage and/or environmental effects, such as UV light and/or soiling.

For example, a polycarbonate sheet coated with the 2-K PU binder used in accordance with the invention as adhesion promoter and with a prepared inorganic coating organically modified in accordance with the teaching of EP-A 947 520 (Example 14) can be protected effectively against mechanical damage and against radiation damage. The protective effect remains fully retained even after intensive weathering. A polycarbonate sheet coated with the coating system described can be exposed to boiling, fully deionized water for several days without any discernible loss of adhesion or optical alteration. After 1 000 hours of weathering in a UV-A test at an intensity of 1.35 W/m^2 (ASTM G 154-97, cycle 4), no optical alteration is observable on either the substrate or on the primer or the inorganic coating.

The drying and curing of the 2-K PU binder used in accordance with the invention can take place between ambient temperature and the softening temperature of the polymeric substrate. For polycarbonate substrates, for example, the curing temperature range is preferably between 20°C and 130°C (Makrolon[®], Bayer AG, Leverkusen, or Lexan[®], GE Plastics, USA) or 20 to 160°C for Apec HT[®] (Bayer AG, Leverkusen) with a cure time of between 1 minute and 60 minutes. More preferably the curing temperature range for Makrolon[®] is between 100°C and 130°C and for Apec HT[®] between 100°C and 160°C with a cure time of between 30 and 60 minutes.

The application conditions and curing conditions of the inorganic coatings are dependent on the particular binder system. The 2-K PU binder used in accordance with the invention and the organically modified inorganic coating can be applied and cured in succession. Likewise possible is a wet-on-wet application, followed by a single cure within the abovementioned temperature and time range.

30

For special applications, a cure at ambient temperature may also be sufficient, where appropriate.

Examples

In the examples below all percentages are by weight.

Coatings additives used were, for example, Baysilone® OL 17 (Bayer AG,
5 Leverkusen), Tinuvin® 292 (Ciba Spezialitätenchemie GmbH, Lampertheim) and/or
Tinuvin® 1130 (Ciba Spezialitätenchemie GmbH, Lampertheim).

Example 1

10 Diethyl N-(3-trimethoxysilylpropyl)aspartate is prepared, in accordance with the
teaching of US-A 5 364 955, Example 5, by reacting equimolar amounts of 3-
aminopropyltrimethoxysilane with diethyl maleate.

Example 2

15

A standard stirring apparatus is charged with 180 g (1 eq NCO) of a 100% HDI
isocyanurate having a viscosity of 1200 mPas (23°C), an average NCO content of
23%, and an NCO functionality of 3.2. At room temperature, with vigorous stirring,
17.55 g (0.05 mol) of diethyl N-(3-trimethoxysilylpropyl)aspartate from Example 1
20 are added dropwise and the mixture is subsequently stirred for one hour. The
resulting adduct has an NCO content of 20%.

Example 3 to 20

25 Same procedure as in Example 2. Table 1 indicates in each case the polyisocyanate
and alkoxysilane used in the amounts employed in each case. The resulting NCO
content of the adduct is indicated in %.

30 Polyisocyanate A	HDI isocyanurate, 90% strength in butyl acetate with a viscosity of 600 mPas (23°C), an average NCO content of 19.6%, an NCO functionality of 3.2.
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- Polyisocyanate B HDI biuret, 75% strength in butyl acetate with a viscosity of 160 mPas (23°C), an average NCO content of 16.5%, and an NCO functionality of 3.8.
- 5 Polyisocyanate C IPDI isocyanurate, 70% strength in butyl acetate with a viscosity of 700 mPas (23°C), an average NCO content of 11.8%, and an NCO functionality of 3.2.
- 10 Alkoxysilane 1: diethyl N-(3-trimethoxysilylpropyl)aspartate from Example 1
- Alkoxysilane 2: N-butyl-3-aminopropyltrimethoxysilane, (Dynasilan® 1189, Degussa-Hüls AG)
- 15 Alkoxysilane 3: bis(trimethoxysilylpropyl)amine, (Silques A-1170, Wite)
- Alkoxysilane 4: N-methyl-3-aminopropyltrimethoxysilane, (Dynasilan® 1110, Degussa-Hüls AG)
- 20 Alkoxysilane 5: 3-mercaptopropyltrimethoxysilane, (Dynasilan® NTNS, Degussa-Hüls AG)

Table 1: Examples 3 to 20

Example	Poly-isocyanate	Initial mass [g]	Alkoxy-silane	Initial mass [g]	NCO content [%]	Remarks * ¹
3	A	216	1	17.55	17.1	---
4	B	255	1	17.55	14.7	---
5	C	178	1	8.78	10.7	---
6	B	50	1	0.7	16.1	---
7	B	50	1	13.8	10.3	---
8	B	100	5	4.7	14.9	
9	B	100	5	9.4	13.5	
10	B	100	5	18.7	11.1	
11	B	100	5	46.7	5.9	60% in BA
12	C	100	2	3.29	10.8	
13	C	100	2	6.5	9.8	
14	C	100	2	13.1	8.3	
15	C	100	2	32.6	3.5	60% in BA
16	B	50	2	2.3	14.9	
17	B	50	4	1.89	15.0	
18	B	100	3	6.69	14.7	
19	C	100	5	3.34	10.8	
20	B	100	1	103.23	1.8	70% in BA

*¹) SC.: solids content in % by weight, BA: butyl acetate

5

Auxiliaries and polyols suitable for the 2-K-PUR binders used in accordance with the invention are assembled in Table 2. The preparation of components B1 to B5 is accomplished by arbitrarily combining the individual components listed in Table 2 in any order and then mixing them at room temperature.

10

Polyol 1: trimethylolpropane

Polyol 2: Desmophen®670 (Bayer AG, Leverkusen), which is a commercial, hydroxyl-containing polyester with a low degree of branching, 80% strength in BA with a hydroxyl content of 3.5%, an acid number of 2 mg KOH/g, and a viscosity of 2800 mPas (23°C)

5

Polyol 3: Desmophen®800 (Bayer AG, Leverkusen), which is a commercial, hydroxyl-containing polyester with a high degree of branching, solvent-free with a hydroxyl content of 8.6%, an acid number of 4 mg KOH/g, and a viscosity of 850 mPas (23°C, 70% MPA)

10

Polyol 4: Desmophen® VPLS 2249/1 (Bayer AG, Leverkusen), which is a commercial branched short-chain polyester, solvent-free, with a hydroxyl content of 16%, an acid number of 2 mg KOH/g, and a viscosity of 1900 mPas (23°C)

15

DAA: diacetone alcohol

Table 2: Polyols and auxiliaries (inventive)

	B 1	B 2	B 3	B 4	B 5
Polyol (X) X = 1, 2, 3, 4	12.3 g (1)	15.4 g (2)	11.6 g (2) 3.1 g (3)	3.9 g (2) 9.2 g (3)	12.3 g (4)
Butyl acetate	3.1 g	-	0.8 g	2.3 g	3.1 g
Baysilone® OL 17 10% strength in DAA	0.2 g	0.2 g	0.2 g	0.2 g	0.2 g
Tinuvin® 292 10% strength in DAA	2.0 g	2.0 g	2.0 g	2.0 g	2.0 g
Tinuvin 1130 10% strength in DAA	2.0 g	2.0 g	2.0 g	2.0 g	2.0 g
Zinc octoate 10% strength in DAA	0.4 g	0.4 g	0.4 g	0.4 g	0.4 g

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	B 1	B 2	B 3	B 4	B 5
DAA	170.5 g	170.5 g	170.5 g	170.5 g	170.5 g
Equivalent weight	692.0 g	6012.0 g	4835.0 g	3521.0 g	1639.0 g

Preparation of the 2-K PU binder used according to the invention as adhesion promoter (primer) (Example 21 to 27)

- 5 A silicon-modified polyisocyanate from Table 1 is combined at room temperature with one of the polyol mixtures B 1 to B 5 from Table 2, in each case in an NCO : OH ratio of 1.2 : 1, and the components are mixed. The 2-K PU binder used according to the invention is ready for application. Corresponding combinations of the polyol mixture B1 to B5 and the silicon-modified polyisocyanates from Table 1
- 10 are possible. Table 3 contains by way of example for all possible combinations arising from Table 1 and Table 2 for the preparation of the 2-K PU binders used according to the invention.

Table 3: 2-K PU binders used according to the invention as adhesion promoters (primers)

Example	Polyisocyanate from Example	Initial mass [g]	Polyol component	Initial mass [g]
21	4	5.7	B 2	100
22	8	48.9	B 1	100
23	12	7.75	B 2	100
24	14	37.3	B 5	100
25	15	30.1	B 3	100
26	18	21	B 5	100
27	12	13.2	B 4	100

Example 28

26.4 g of a 75% strength solution of a hydroxy-functional polyacrylate in xylene having a hydroxyl content of 2.8%, an acid number of 2 mg KOH/g and a viscosity of 3 500 mPas (23°C), and also 0.94 g of baysilone oil OL 17 (10% strength in xylene), 0.35 g of DBTL (dibutyl tin laurate, 10% strength in xylene) and 25 g of xylene are mixed homogeneously. Into this mixture, 12.5 g of silicon-modified isocyanate component from Example 4 are stirred.

10 Application Examples

The following examples serve to demonstrate the effectiveness of the 2-K PU binders used in accordance with the invention as adhesion promoters (primers).

15 Example 29

Adhesion promoter for a hydrophobic/oleophobic, silicon-containing coating

A steel panel coated with a commercial adhesion promoter (Sigma Universal Primer® 7417, Sigmakalan, NL) and epoxy anticorrosion varnish (Sigma Multiguard®, Sigmakalan, NL) is coated with the 2-K PU binder from Example 28 used in accordance with the invention as adhesion promoter in a dry film thickness of about 15 µm, and the coating is dried at room temperature for 24 hours.

25 Applied to the adhesion promoter is an organically modified inorganic coating material composed of 64.6% by weight of an ethoxy-functional siloxane prepared according to Example 2 in WO 98/52992, 12.9% by weight of a 50% dispersion of a polycondensation product of tetraethoxysilane in n-butanol, 15.5% by weight of an α,ω-hydroxy-functional polydimethylsiloxane having an OH content of about 6%,
30 1.3% by weight of 3-mercaptopropyltriethoxysilane and 5.7% by weight of an approximately 2% strength solution of para-toluenesulphonic acid in n-butanol, in a dry film thickness of approximately 40 µm, and this coating is likewise dried at room temperature for 24 hours.

The resulting protective coating exhibits very good adhesion to the polymeric substrate. It is stable to weathering and protects effectively against soiling. The coating is not wetted by a permanent marker from Edding (Edding® 850). 24 hours after its application, the marker can be removed without residue using a cloth, without the aid of cleaning product.

Adhesive properties of the 2-K PU binder used in accordance with the invention as adhesion promoter (primer) on polycarbonate

10 **Example 30**

The 2-K PU binder of Example 22 in Table 3, used according to the invention as an adhesion promoter, was applied by spin coating in a film thickness of about 0.2 µm to a Makrolon® sheet and was cured at 130°C for 60 minutes. Subsequently a silicon-containing coating which is described in EP-A 0 947 520 Example 14 was applied by spin coating in a film thickness of 3 µm and was cured at 130°C for 60 minutes.

Example 31

20 Same procedure as in Example 30. However, the 2-K PU binder used in accordance with the invention as adhesion promoter, from Example 23 in Table 3, was applied by spin coating in a film thickness of about 0.2 µm.

Comparative Example 1

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Same procedure as in Example 30 and 31. Instead of the 2-K PU binder used in accordance with the invention as adhesion promoter, 3-aminopropyltrimethoxysilane, as a prior art primer for polycarbonate, was applied by spin coating in a film thickness of about 0.2 µm.

Comparative Example 2

Same procedure as in Example 30 and 31. A non-silicon-modified polyisocyanate was used as crosslinker. For this purpose, 100 g of the polyol component B 2 from Table 2 were stirred together with 7.2 g of a 70% strength solution in butyl acetate of an IPDI isocyanurate with an average NCO content of 11.8% and an NCO functionality of 3.2 and a viscosity of 700 mPas (23°C) in an NCO : OH ratio of 1.2 : 1 and applied by spin coating in a film thickness of approximately 0.2 µm.

Comparative Example 3

Same procedure as in Example 30 and 31. A non-silicon-modified polyisocyanate was used as crosslinker. For this purpose, 100 g of the polyol component B 2 from Table 2 were stirred together with 5.1 g of a 75% strength solution in butyl acetate of an HDI biuret with an average NCO content of 16.5% and an NCO functionality of 3.8 and a viscosity of 160 mPas (23°C) in an NCO : OH ratio of 1.2 : 1 and applied by spin coating in a film thickness of approximately 0.2 µm.

The Makrolon® sheets coated in accordance with Examples 30 and 31 and also Comparative Examples 1 to 3 were tested for adhesion before and after weathering. For this purpose, one plate in each case was stored in demineralized water at 100°C for 8 hours. A further sample was stored in demineralized water at 65°C for 14 days. Additionally, one plate in each case was weathered in accordance with ASTM G 154-97 cycle 4 for 1000 h. After weathering, the adhesion was tested by means of cross-cut DIN EN ISO 2409. The results of the cross-cut test after weathering are assembled in Table 4.

Table 4: Cross-cut to DIN EN ISO 2409 after weathering

	Example 30	Example 31	Comparative Example 1	Comparative Example 2	Comparative Example 3
Base line adhesion (before weathering)	0	0	0	5	0
Adhesion after 8 h of storage in demineralized water at 100°C	0	0	5	---	5
Adhesion after 14 d of storage in demineralized water at 65°C	0	0	5	---	5
Adhesion after 1000 h weathering to ASTM G 154-97 cycle 4	0	0	---	---	---

Cross-cut index:

- absolutely no delamination (0)
- 5 complete delamination (5)
- not carried out (---)

From Table 4 it is apparent that the 2-K PU binder used in accordance with the invention as adhesion promoter results in good adhesion and excellent weathering stability of the organically modified inorganic coatings on polymeric substrates such as, for example, polycarbonate, polymethyl methacrylate or polyurethane. 3-aminopropyltrimethoxysilane, a prior art primer for polycarbonate, leads to complete delamination on storage in demineralized water. Adhesion promoters based on polyisocyanates which have not been inventively modified either have inadequate base adhesion or exhibit a much lower resistance under weathering/water storage than the adhesion promoters of the invention.

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CLAIMS:

1. Use of a solventborne two-component polyurethane binder, comprising

(1) a curing component (A) comprising an adduct of at least one
 5 organic polyisocyanate (B) having an average NCO functionality of from 2.5 to 5.0 and an isocyanate content of from 8 to 27% by weight and an alkoxysilane (C) having at least one isocyanate-reactive group of the general formula (I):



in which:

10 Q is an isocyanate-reactive group,

Z is a linear or branched C₁-C₁₂ alkylene group,

X is a hydrolyzable group,

Y is identical or different C₁-C₄ alkyl groups, and

a is an integer from 1 to 3; and

15 (2) an isocyanate-reactive film-forming resin (D),

wherein the polyisocyanate components, binder components or both are employed in a form in which they are diluted with diacetone alcohol or a mixture of diacetone alcohol with butyl acetate, ethyl acetate or both butyl acetate and ethyl acetate,

20 as an adhesion promoter.

2. The use according to claim 1, wherein X is C₁-C₄ alkoxy.

3. The use according to claim 1 or 2, wherein the ratio of the isocyanate-reactive groups of the film-forming resin (D) to the isocyanate groups of the curing agent (A) lies between 0.5:1 to 2:1.

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4. The use according to any one of claims 1 to 3, wherein the at least one polyisocyanate (B) has an average NCO functionality of from 2.5 to 4.5 and the isocyanate group content of from 11.0 to 24.0% by weight.
5. The use according to any one of claims 1 to 4, wherein the at least one organic polyisocyanate (B) comprises a polyisocyanate or a mixture of polyisocyanates containing an aliphatic and/or cycloaliphatic group bonded to the isocyanate groups.
6. The use according to any one of claims 1 to 4, wherein the at least one organic polyisocyanate (B) comprises a polyisocyanate or a polyisocyanate mixture having biuret or isocyanurate structure based on HDI, IPDI and/or 4,4'-diisocyanatodicyclohexylmethane.
7. The use according to any one of claims 1 to 6, wherein the at least one organic polyisocyanate (B) is reacted with the alkoxysilane (C) in a molar NCO/Q ratio of 1:0.01 to 0.75, wherein Q is as defined in claim 1.
8. The use according to any one of claims 1 to 7, wherein the alkoxysilane (C) is a compound of the general formula (I):



in which:

Q is OH, SH or NHR_1 , wherein R_1 is a C_1 - C_{12} alkyl group, a C_6 - C_{20} aryl group or $-\text{Z-SiX}_a\text{Y}_{3-a}$,

Z is a linear or branched C_1 - C_4 alkylene group,

X is a C_1 - C_4 alkoxy group,

Y is identical or different C_1 - C_4 alkyl groups, and

a is an integer from 1 to 3.

9. The use according to any one of claims 1 to 8, wherein the adhesion promoter is applied to a substrate and subsequently a coating is applied.

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10. The use according to claim 9, wherein the substrate is a polymeric substrate, a metal substrate or a glass substrate.

11. The use according to claim 10, wherein the polymeric substrate is polycarbonate, polymethyl methacrylate, polystyrene, polyvinylcyclohexane or a
5 copolymer thereof, polyvinylchloride or a blend thereof.

12. The use according to any one of claims 9 to 11, wherein the coating is an inorganic coating, an organic coating or an inorganic-organic hydride coating.

13. The use according to claim 12, wherein the inorganic coating
10 comprises silicon.

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