

Two-component systems for producing flexible coatings

The present invention relates to two-component coating systems for producing flexible coatings. The coating systems comprise polyurethane prepolymers with allophanate structures and also amino-functional polyaspartic esters as curing agents.

5 Polyurethane-based or polyurea-based two-component coating systems are known and are used in the art. In general they include a liquid polyisocyanate component and a liquid, isocyanate-reactive component. Reaction of polyisocyanates with amines as an isocyanates-reactive component produces highly crosslinked polyurea coatings. Primary amines and isocyanates, however, usually react very rapidly with one another. Typical potlives or gelling times often amount only to several
10 seconds to a few minutes. Consequently polyurea coatings of this kind can be applied not manually but only with special spraying apparatus. Such coatings, however, possess excellent physical properties.

One method from the literature of reducing the reactivity is to use prepolymers having a low NCO content. Through the use of NCO-functional prepolymers in combination with amines it is possible
15 to produce flexible polyurea coatings.

US-A 3 428 610 and US-A 4 463 126 disclose the preparation of polyurethane/polyurea elastomers by curing NCO-functional prepolymers with aromatic diamines. These are preferably diprimary aromatic diamines, having at least one alkyl substituent of 2-3 carbon atoms positioned ortho to each amino group, and possibly also having methyl substituents in further positions ortho to the
20 amino groups, such as, for example, diethyltolylidiamine (DETDA).

US-A 4 463 126 describes a process for producing solvent-free elastic coatings which involves curing NCO prepolymers based on isophorone diisocyanate (IPDI) and polyether polyols at room temperature using sterically hindered diprimary aromatic diamines.

A disadvantage associated with such systems is that the aromatic diamines have a propensity
25 towards severe yellowing.

A further option for retarding the reaction between polyisocyanates and amines is to use secondary amines. EP-A 403 921 and US-A 5 126 170 disclose the formation of polyurea coatings by reaction of polyaspartic esters with polyisocyanates. Polyaspartic esters possess low viscosity and reduced reactivity towards polyisocyanates and can therefore be used for preparing solvent-free
30 coating materials having extended potlives. An additional advantage of polyaspartic esters is that the products are colourless.

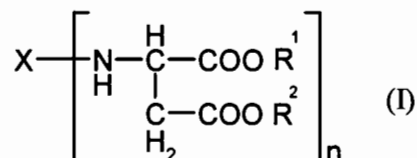
Colourless aliphatic polyisocyanate prepolymers based on polyether polyols, however, cure extremely slowly with polyaspartic esters, and the coatings often possess a tacky surface.

It was an object of the present invention, therefore, to provide two-component coating materials for producing polyurea coatings, said materials having potlives long enough to enable even manual application and permitting the production of flexible coatings which are both clear and colourless and have good performance data such as elasticity and hardness.

This object has now been achieved through the combination of specific allophanate polyisocyanates with polyaspartic esters.

The invention accordingly provides two-component coating systems at least comprising

- A) a polyisocyanate prepolymer having polyether groups attached via allophanate groups and
- B) amino-functional polyaspartic esters of the general formula (I)



in which

X is an n-valent organic radical obtained by removing the primary amino groups of an n-valent polyamine,

R¹ and R² are identical or different organic radicals which are inert towards isocyanate groups under the reaction conditions and

n is a whole number of at least 2.

The allophanates used in component A) are obtainable by reacting

A1) one or more aliphatic and/or cycloaliphatic polyisocyanates with

A2) one or more polyhydroxy compounds, at least one being a polyether polyol,

to give an NCO-functional polyurethane prepolymer and then subsequently subjecting its urethane groups thus formed to partial or complete allophanatization with addition of

A3) polyisocyanates, which can be different from those from A1), and

A4) catalysts and

A5) optionally stabilizers.

5 Examples of suitable aliphatic and cycloaliphatic polyisocyanates A1) are diisocyanates or triisocyanates such as butane diisocyanate, pentane diisocyanate, hexane diisocyanate (hexamethylene diisocyanate, HDI), 4-isocyanatomethyl-octane 1,8-diisocyanate (triisocyanatononane, TIN) or cyclic systems, such as 4,4'-methylenebis(cyclohexyl isocyanate), 3,5,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane (isophorone diisocyanate, IPDI) and also ω,ω' -diisocyanato-1,3-dimethylcyclohexane (H_6 XDI).

10 In components A1) to A3) it is preferred to use hexane diisocyanate (hexamethylene diisocyanate, HDI), 4,4'-methylenebis(cyclohexyl isocyanate) and/or 3,5,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane (isophorone diisocyanate, IPDI) as polyisocyanates. An especially preferred polyisocyanate is HDI.

In A1) and A3) it is preferred to use polyisocyanates of the same type.

15 As polyhydroxy compounds of component A2) it is possible to use all of the polyhydroxy compounds known to the skilled person that have, preferably, an average OH functionality of greater than or equal to 1.5, at least one of the compounds contained in A2) necessarily being a polyether polyol.

20 Suitable polyhydroxy compounds which can be used in A2) are low molecular weight diols (e.g. 1,2-ethanediol, 1,3- and 1,2-propanediol, 1,4-butanediol), triols (e.g. glycerol, trimethylolpropane) and tetraols (e.g. pentaerythritol), polyether polyols, polyester polyols, polycarbonate polyols and polythioether polyols. In A2) it is preferred to use, as polyhydroxy compounds, exclusively substances of the aforementioned kind that are based on polyether.

25 The polyether polyols used in A2) preferably have number-average molecular weights M_n of 300 to 20 000 g/mol, with particular preference 1000 to 12 000 g/mol, with very particular preference 2000 to 6000 g/mol.

They further possess preferably an average OH functionality of ≥ 1.9 , with particular preference ≥ 1.95 .

Polyether polyols of this kind are obtainable in a conventional manner by alkoxylation of suitable starter molecules with base catalysis or using double metal cyanide (DMC) compounds.

30 Particularly suitable polyether polyols of component A2) are those of the aforementioned kind having an unsaturated end group content of less than or equal to 0.02 milliequivalents per gram of

polyol (meq/g), preferably less than or equal to 0.015 meq/g, with particular preference less than or equal to 0.01 meq/g (determination method: ASTM D2849-69).

5 Polyether polyols of this kind are preparable in conventional manner by alkoxylation of suitable starter molecules, in particular with use of double metal cyanide catalysts (DMC catalysis). This is described, for example, in US-A 5 158 922 (e.g. Example 30) and EP-A 0 654 302 (p. 5, l. 26 to p. 6, l. 32).

10 Examples of suitable starter molecules for the preparation of polyether polyols are simple polyols of low molecular weight, water, organic polyamines having at least two N-H bonds, or any desired mixtures of such starter molecules. Alkylene oxides particularly suitable for the alkoxylation are ethylene oxide and/or propylene oxide, which can be used in any order or else in a mixture for the alkoxylation.

15 Preferred starter molecules for the preparation of polyether polyols by alkoxylation, in particular by the DMC process, are, in particular, simple polyols such as ethylene glycol, propylene 1,3-glycol and butane-1,4-diol, hexane-1,6-diol, neopentyl glycol, 2-ethylhexane-1,3-diol, glycerol, trimethylolpropane, pentaerythritol, and also low molecular weight, hydroxyl-containing esters of such polyols with dicarboxylic acids of the type exemplified below, or low molecular weight ethoxylation or propoxylation products of such simple polyols or any desired mixtures of modified or unmodified alcohols of this kind.

20 The preparation of the polyurethane prepolymers, containing isocyanate groups, as intermediates is accomplished by reaction of the polyhydroxy compounds of component A2) with excess amounts of the polyisocyanates from A1). The reaction takes place in general at temperatures from 20 to 140°C, preferably at 40 to 100°C, with the use where appropriate of catalysts known per se from polyurethane chemistry, such as tin soaps, for example, e.g. dibutyltin dilaurate, or tertiary amines, e.g. triethylamine or diazabicyclooctane.

25 The allophanatization then takes place thereafter by reaction of the polyurethane prepolymers containing isocyanate groups with polyisocyanates A3), which can be the same as or different from those of component A1), with the addition of suitable catalysts A4) for the allophanatization. Typically thereafter the acidic additives of component A5) are added for stabilization and excess polyisocyanate is removed from the product by means, for example, of thin-film distillation or
30 extraction.

The molar ratio of the OH groups of the compounds of component A2) to the NCO groups of the polyisocyanates from A1) and A3) is preferably 1:1.5 to 1:20, with particular preference 1:2 to 1:15, with very particular preference 1:2 to 1:10.

Zinc(II) compounds are used with preference as catalysts in A4), these being, with particular preference, zinc soaps of relatively long-chain, branched or unbranched, aliphatic carboxylic acids. Preferred zinc(II) soaps are those based on 2-ethylhexanoic acid and also on the linear, aliphatic C₄ to C₃₀ carboxylic acids. Very particularly preferred compounds of component A4) are Zinc(II) bis-
5 (2-ethylhexanoate), Zinc(II) bis(n-octoate), Zinc(II) bis(stearate) or mixtures thereof.

These allophanatization catalysts are employed typically in amounts from 5 ppm up to 5% by weight, based on the reaction mixture as a whole. Preference is given to using 5 to 500 ppm of the catalyst, with particular preference 20 to 200 ppm.

If desired it is also possible to use additives having a stabilizing action, before, during or after the
10 allophanatization. These may be acidic additives such as Lewis acids (electron deficiency compounds) or Broenstedt acids (protonic acids) or compounds of the kind which release such acids on reaction with water

These are, for example, organic or inorganic acids or else neutral compounds such as acid halides or esters which react with water to give the corresponding acids. Mention may be made here in
15 particular of hydrochloric acid, phosphoric acid, phosphoric esters, benzoyl chloride, isophthaloyl dichloride, p-toluenesulphonic acid, formic acid, acetic acid, dichloroacetic acid and 2-chloropropionic acid.

The aforementioned acid additives can also be used to deactivate the allophanatization catalyst. Furthermore, they improve the stability of the allophanates prepared in accordance with the
20 invention, having this effect, for example, under thermal load in the course of thin-film distillation or else after the preparation, during storage of the products.

The acidic additives are generally added in an amount at least sufficient for the molar ratio of the acidic centres of the acidic additive and of the catalyst to amount to at least 1:1. It is nevertheless preferred to add an excess of the acidic additive.

25 Where acidic additives are used at all they are preferably organic acids such as carboxylic acids or acid halides such as benzoyl chloride or isophthaloyl dichloride.

Where excess diisocyanate is to be separated off, thin-film distillation is the preferred method and is carried out generally at temperatures from 100 to 160°C under a pressure of 0.01 to 3 mbar. The residual monomer content thereafter is preferably less than 1% by weight, with particular
30 preference less than 0.5% by weight (diisocyanate).

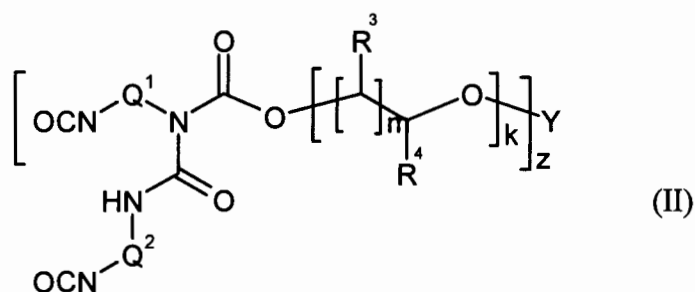
The process steps overall can be carried out optionally in the presence of inert solvents. By inert solvents are meant those which do react with the reactants under the prevailing reaction conditions.

Examples are ethyl acetate, butyl acetate, methoxypropyl acetate, methyl ethyl ketone, methyl isobutyl ketone, toluene, xylene, aromatic or (cyclo-) aliphatic hydrocarbon mixtures or any desired mixtures of such solvents. With preference, however, the reactions according to the invention are carried out in solvent-free form.

5 The addition of the components involved may take place both during the preparation of the prepolymers containing isocyanate groups and during allophanatization, in any order. It is nevertheless preferred to add the polyether polyol A2) to the initial charge of polyisocyanate of components A1) and A3), and finally to add the allophanatization catalyst A4).

In one preferred embodiment of the invention the polyisocyanates of components A1) and A3) are charged to a suitable reaction vessel and this initial charge is heated to 40 to 100°C, with stirring where appropriate. After the desired temperature has been reached the polyhydroxy compounds of component A2) are then added with stirring, and stirring is continued until the NCO content has reached or is slightly below the theoretical NCO content of the polyurethane prepolymer to be expected in accordance with the chosen stoichiometry. At this point the allophanatization catalyst A4) is added and the reaction mixture is heated at 50 and 100°C until the NCO content has reached or is slightly below the desired NCO content. Following the addition of acidic additives as stabilizers, the reaction mixture is cooled or passed on directly for thin-film distillation. There the excess polyisocyanate is separated off at temperatures of 100 to 160°C under a pressure of 0.01 to 3 mbar down to a residual monomer content of less than 1%, preferably less than 0.5%. Following the thin-film distillation it is possible if desired to add further stabilizer.

Such allophanates, used in the two-component coating systems claimed, correspond typically to the general formula (II),



in which

25 Q¹ and Q² independently of one another are the radical of a linear and/or cyclic aliphatic diisocyanate of the type stated, preferably -(CH₂)₆-,

R^3 and R^4 independently of one another are hydrogen or a C_1 - C_4 alkyl radical, R^3 and R^4 being preferably hydrogen and/or methyl groups and it being possible in each repeating unit k for the definition of R^3 and R^4 to be different,

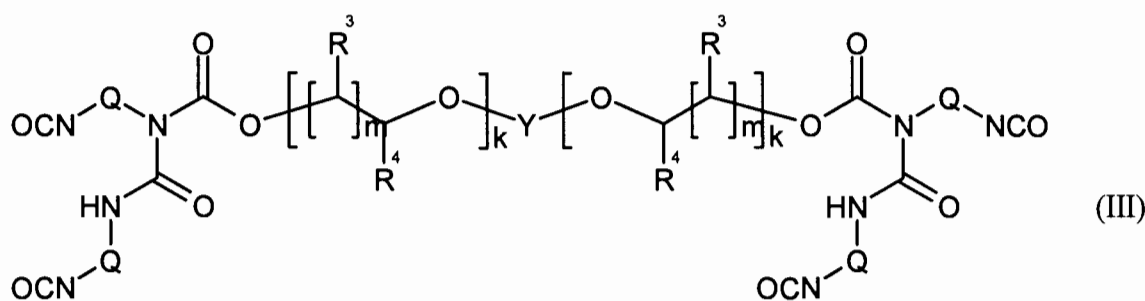
Y is the radical of a starter molecule of the type stated, having a functionality of 2 to 6, and hence

z is a number from 2 to 6, which as a result of the use of different starter molecules need not of course be a whole number, and also

k corresponds preferably to a number of monomer units sufficient for the number-average molecular weight of the polyether on which the structure is based to be 300 to 20 000 g/mol, and

m is 1 or 3.

Allophanates obtained correspond preferably to the general formula (III),



in which

Q is the radical of a linear and/or cyclic aliphatic diisocyanate of the type stated, preferably $-(CH_2)_6-$,

R^3 and R^4 independently of one another are hydrogen or a C_1 - C_4 alkyl radical, R^3 and R^4 being preferably hydrogen and/or methyl groups and it being possible in each repeating unit m for the definition of R^3 and R^4 to be different,

Y is the radical of a difunctional starter molecule of the type stated, and

k corresponds to a number of monomer units sufficient for the number-average molecular weight of the polyether on which the structure is based to be 300 to 20 000 g/mol, and

m is 1 or 3.

Since polyols based on polymerized ethylene oxide, propylene oxide or tetrahydrofuran are generally used to prepare the allophanates of the formulae (II) and (III), in the case of $m = 1$ in the formulae (II) and (III) at least one radical of R^3 and R^4 is with particular preference hydrogen, and in the case of $m = 3$ R^3 and R^4 are hydrogen.

- 5 The allophanates used in accordance with the invention in A) typically have number-average molecular weights of 700 to 50 000 g/mol, preferably 1500 to 8000 g/mol and with particular preference 1500 to 4000 g/mol.

The allophanates used in accordance with the invention in A) typically have viscosities at 23°C of 500 to 100 000 mPas, preferably 500 to 50 000 mPas and with particular preference from 1000 to 10 7500 mPas, with very particular preference from 1000 to 3500 mPas.

The group X in formula (I) of the polyaspartic esters of component B) is based preferably on an n-valent polyamine selected from the group consisting of ethylenediamine, 1,2-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 2,5-diamino-2,5-dimethylhexane, 2,2,4- and/or 2,4,4-trimethyl-1,6-diaminohexane, 1,11-diaminoundecane, 1,12-diaminododecane, 1-amino-3,3,5-trimethyl-5-aminomethylcyclohexane, 2,4- and/or 2,6-hexahydrotolylenediamine, 2,4'- and/or 4,4'-diaminodicyclohexylmethane, 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane, 2,4,4'-triamino-5-methyldicyclohexylmethane and polyether polyamines with aliphatically attached primary amino groups, having a number-average molecular weight M_n of 148 to 6000 g/mol.

With particular preference the group X is based on 1,4-diaminobutane, 1,6-diaminohexane, 2,2,4- and/or 2,4,4-trimethyl-1,6-diaminohexane, 1-amino-3,3,5-trimethyl-5-aminomethylcyclohexane, 4,4'-diaminodicyclohexylmethane or 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane.

In respect of the radicals R^1 and R^2 the phrase "inert towards isocyanate groups under the reaction conditions" means that these radicals do not have groups containing Zerewitinoff-active hydrogen (CH acidic compounds; cf. Römpp Chemie Lexikon, Georg Thieme Verlag Stuttgart) such as OH, NH or SH.

R^1 and R^2 independently of one another are preferably C_1 to C_{10} alkyl radicals, with particular preference methyl or ethyl radicals.

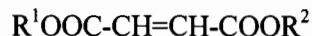
Where X is based on 2,4,4'-triamino-5-methyldicyclohexylmethane preferably $R^1 = R^2 =$ ethyl.

In formula (I) n is preferably a whole number from 2 to 6, with particular preference 2 to 4.

- 30 The amino-functional polyaspartic esters B) are prepared conventionally by reacting the corresponding primary polyamines of the formula



with maleic or fumaric esters of the general formula



Suitable polyamines are the diamines specified above as a basis for the group X.

- 5 Examples of suitable maleic or fumaric esters are dimethyl maleate, diethyl maleate, dibutyl maleate and the corresponding fumaric esters.

10 The preparation of the amino-functional polyaspartic esters B) from the stated starting materials takes place preferably within the temperature range from 0 to 100°C, the starting materials being employed in proportions such that for each primary amino group there is at least one, preferably exactly one, olefinic double bond; after the reaction it is possible, if desired, to separate off, by distillation, starting materials employed in excess. The reaction may take place in bulk or in the presence of suitable solvents such as methanol, ethanol, propanol or dioxane or mixtures of such solvents.

15 In the two-component coating systems of the invention the ratio of free or blocked amino groups to free NCO groups is preferably 0.5:1 to 1.5:1, with particular preference 1:1 to 1.5:1.

To prepare the two-component coating systems of the invention the individual components are mixed with one another.

20 The stated coating materials may be applied to surfaces by the conventional techniques such as spraying, dipping, flooding, rolling, brushing or pouring. After flashing off to remove any solvents present, the coatings then cure under ambient conditions or else at higher temperatures of, for example, 40 to 200°C.

The stated coating materials can be applied for example to metals, plastics, ceramic, glass and also natural substances, it being possible for the stated substrates to have been subjected beforehand to any pretreatment that may be necessary.

Examples:

The NCO contents were determined by back-titrating di-n-butylamine added in excess with hydrochloric acid. The viscosities were determined using a rotation viscometer from Haake at 23°C.

5 Unless indicated otherwise, all percentages are by weight.

Preparation of prepolymer 1

2520.7 g of hexane 1,6-diisocyanate were first admixed with 90 mg of isophthaloyl dichloride and then the mixture was heated to 100°C with stirring. At that point, over the course of 3 hours, 1978.5 g of a polypropylene glycol were added which had been prepared by means of DMC
10 catalysis (base-free) (unsaturated groups content < 0.01 meq/g, molar weight 2000 g/mol, OH number 56, theoretical functionality 2). The reaction mixture was subsequently heated at 100°C until an NCO content of 26.1% had been reached. Then the temperature was lowered to 90°C and the reaction mixture, following the addition of 360 mg of zinc(II) bis(2-ethylhexanoate), was stirred until the NCO content was 24.3%. After 360 mg of isophthaloyl dichloride had been added,
15 the excess hexane 1,6-diisocyanate was removed by means of thin-film distillation at 0.5 mbar and 140°C.

This gave a clear, colourless product having an NCO content of 5.9%, a viscosity of 2070 mPas (23°C) and a residual free HDI content of < 0.03%.

Preparation of prepolymer 2

20 1003.4 g of hexane 1,6-diisocyanate were first admixed with 40 mg of isophthaloyl dichloride and then the mixture was heated to 100°C with stirring. At that point, over the course of 3 hours, 796.3 g of a polytetramethylene glycol were added (= polytetrahydrofuran, molar weight 2000 g/mol, OH number 56, theoretical functionality 2). The reaction mixture was subsequently heated at 100°C until an NCO content of 26.0% had been reached. Then the temperature was
25 lowered to 90°C and the reaction mixture, following the addition of 140 mg of zinc(II) bis(2-ethylhexanoate), was stirred until the NCO content was 24.2%. After 140 mg of isophthaloyl dichloride had been added, the excess hexane 1,6-diisocyanate was removed by means of thin-film distillation at 0.5 mbar and 140°C.

30 This gave a clear, colourless product having an NCO content of 5.9%, a viscosity of 17 300 mPas (23°C) and a residual free HDI content of 0.06%.

Preparation of prepolymer 3

77.3 g of hexane 1,6-diisocyanate were first admixed with 4 mg of isophthaloyl dichloride and then the mixture was heated to 100°C with stirring. At that point, over the course of 3 hours, 122.7 g of a polypropylene glycol were added which had been prepared by means of DMC catalysis (base-free) (unsaturated groups content < 0.01 meq/g, molar weight 4000 g/mol, OH number 28, theoretical functionality 2). The reaction mixture was subsequently heated at 100°C until an NCO content of 18.0% had been reached. Then the temperature was lowered to 90°C and the reaction mixture, following the addition of 20 mg of zinc(II) bis(2-ethylhexanoate), was stirred until the NCO content was 16.7%. After 20 mg of isophthaloyl dichloride had been added, the excess hexane 1,6-diisocyanate was removed by means of thin-film distillation at 0.7 mbar and 140°C.

This gave a clear, colourless product having an NCO content of 3.2%, a viscosity of 3189 mPas (23°C) and a residual free HDI content of < 0.03%.

Preparation of prepolymer 4 (comparative example)

At 100°C 321.4 g of hexane 1,6-diisocyanate were admixed over the course of 5 hours, with stirring, with 378.4 g of a polypropylene glycol which had been prepared by means of DMC catalysis (base-free) (unsaturated groups content < 0.01 meq/g, molar weight 2000 g/mol, OH number 56, theoretical functionality 2). Thereafter the mixture was heated at 100°C with stirring until an NCO content of 20.7% was reached. Following the addition of 140 mg of dibutyl phosphate, finally, the excess hexane 1,6-diisocyanate was removed by means of thin-film distillation at 0.5 mbar and 140°C.

This gave a clear, colourless product having an NCO content of 3.15%, a viscosity of 1596 mPas (23°C) and a residual free HDI content of < 0.03%.

Allophanate 1 (comparative example)

An allophanate was used which was prepared starting from a primary alcohol and was based on HDI, and which had an NCO content of 19.7% and a viscosity of 415 mPas (23°C).

Preparation of polyaspartic ester 1

344 g (2 mol) of diethyl maleate were added dropwise at 50°C with stirring to 210 g (2 eq.) of 4,4'-diaminodicyclohexylmethane. When addition was complete the mixture was stirred at 60°C under an N₂ atmosphere for 90 h, with dewatering at 1 mbar during the last two hours. This gave a liquid product having an equivalent weight of 277 g.

Preparation of polyaspartic ester 2

344 g (2 mol) of diethyl maleate were added dropwise at 50°C with stirring to 238 g (2 eq.) of 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane. When addition was complete the mixture was stirred at 60°C under an N₂ atmosphere for 90 h, with dewatering at 1 mbar during the last two hours. This gave a liquid product having an equivalent weight of 291 g.

5 Production of coatings

Prepolymers 1 and 2 and allophanate 1 (comparative example) were mixed at room temperature with the amino-functional polyaspartic esters 1 and 2 respectively, observing an NCO/NH ratio of 1.05:1. Corresponding films were then applied to a glass plate using a 150 µm doctor. The composition and properties of the coatings are summarized in Table 1.

10 Table 1: Examples 1 to 6 - Compositions and film properties

Examples	1	2	3	4	5	6
Polyaspartic ester 1 [g]	27.9	-	27.9	-	41.4	43.5
Polyaspartic ester 2 [g]	-	29.0	-	29.0		
Prepolymer 1 [g]	70.0	70.0	-	-		
Prepolymer 2 [g]	-	-	75.0	75.0		
Allophanate 1 [g]					33.6	33.6
NH:NCO	1:1.05	1:1.05	1:1.05	1:1.05	1:1.05	1:1.05
Potlife	24 min	5 h 10 min	38 min	6 h 18 min	10 min	10 min
Pendulum hardness: (150 µm wet film)					n.d.	n.d.
After 7d	32"	40"	49"	56"	n.d.	n.d.
Shore hardness D: DIN 53505					n.d.	n.d.
After 7d	27	18	16	13	n.d.	n.d.
Tensile strength ISO EN 527:					n.d.	n.d.
Breaking stress: (MPa)	2.4	1.6	1.1	1.0	n.d.	n.d.
std. dev.	0.3	0.01	0.1	0.06	n.d.	n.d.
Nominal breaking extension: (%)	51.8	65.1	45.6	57.6	n.d.	n.d.
std. dev.	11.5	5.5	4.7	4.8	n.d.	n.d.
Tear propagation tests DIN 53515:					n.d.	n.d.
(N/mm)	3.3	2.3	1.9	1.5	n.d.	n.d.
std. dev.	0.3	0.4	0.4	0.2	n.d.	n.d.

n.d. not determined; potlife is the time within which the compositions can still be processed to a film

15 The prepolymers 1 and 2 containing allophanate groups are based on building blocks which are in principle the same. On the basis of their high compatibility, high functionality and good flexibilizing properties, films were obtained which within 24 h were non-tacky, flexible, tough and clear.

With allophanate 1, on the other hand, curing was very rapid, but the films obtained were so brittle that it was impossible to determine any mechanical properties.

Curing tests

5 The prepolymers 1, 3 and 4 (comparative example) were mixed at room temperature with the amino-functional polyaspartic ester 1, observing an NCO/NH ratio of 1.05:1. After the mixing, the clear compositions were finally cast into films 3 mm thick. The composition and the curing behaviour of the films are summarized in Table 2.

Table 2: Examples 7 to 9

Examples	7	8	9
Polyaspartic ester 1 [g]	18.4	7.4	9.2
Prepolymer 1 [g]	49.3	-	
Prepolymer 3 [g]	-	36.8	
Prepolymer 4 [g]			45,2
NH:NCO	1:1.05	1:1.05	1:1.05
Potlife [min]	35	60	150
Curing (after 24 h)	yes	yes	no

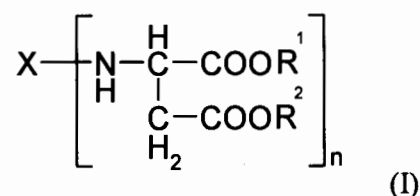
10 Whereas the prepolymers 1 and 3 containing allophanate groups gave clear, flexible and tack-free films after 24 h, the prepolymer 4 (without allophanate groups) did not exhibit complete curing (same NCO content as prepolymer 3).

Claims

1. Two-component coating systems at least comprising

A) a polyisocyanate prepolymer having polyether groups attached via allophanate groups and

5 B) amino-functional polyaspartic esters of the general formula (I)



in which

X is an n-valent organic radical obtained by removing the primary amino groups of an n-valent polyamine,

10 R¹ and R² are identical or different organic radicals which are inert towards isocyanate groups under the reaction conditions and

n is a whole number of at least 2.

2. Two-component coating systems according to Claim 1, characterized in that the allophanates used in A) are prepared by reacting

15 A1) one or more aliphatic and/or cycloaliphatic polyisocyanates with

A2) one or more polyhydroxy compounds, at least one being a polyether polyol,

to give an NCO-functional polyurethane prepolymer and then subsequently subjecting its urethane groups thus formed to partial or complete allophanatization with addition of

A3) polyisocyanates, which can be different from those from A1), and

20 A4) catalysts and

A5) optionally stabilizers.

3. Two-component coating systems according to Claim 2, characterized in that the allophanates used in A) are prepared using, in components A1) and A3), hexane diisocyanate (hexamethylene diisocyanate, HDI), 4,4'-methylenebis(cyclohexyl isocyanate)

and/or 3,5,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane (isophorone diisocyanate, IPDI) as polyisocyanates.

4. Two-component coating systems according to Claim 2 or 3, characterized in that polyisocyanates of the same type are used in A1) and A3).
5. Two-component coating systems according to any one of Claims 2 to 4, characterized in that zinc(II) compounds are used as catalysts for the allophanatization in A4).
6. Two-component coating systems according to Claim 5, characterized in that zinc(II) compounds used are zinc(II) bis(2-ethylhexanoate), zinc(II) bis(n-octoate), zinc(II) bis(stearate) or mixtures thereof.
7. Two-component coating systems according to any one of Claims 2 to 6, characterized in that polyether polyols are used exclusively in A2), these polyols having number-average molecular weights M_n of 2000 to 6000 g/mol, an average OH functionality of ≥ 1.95 and a degree of unsaturated end groups of less than or equal to 0.01 meq/g in accordance with ASTM D2849-69.
8. Two-component coating systems according to any one of Claims 2 to 7, characterized in that the molar ratio of the OH groups of the compounds of component A2) to the NCO-groups of the polyisocyanates from A1) and A3) is 1:2 to 1:10.
9. Two-component coating systems according to any one of Claims 2 to 8, characterized in that stabilizers used in A5) are organic or inorganic acids, acid halides or esters.
10. Coatings obtainable from two-component coating systems according to any of one of Claims 1 to 9.
11. Substrates coated with coatings according to Claim 10.