

Composition for producing polyurea coatings

The invention relates to innovative compositions comprising polyisocyanates containing allophanate groups and polyamines, preferably aromatic diamines, and optionally further polyisocyanates, preferably polyisocyanates containing uretdione groups, and also their use for producing quick-curing polyurea coatings.

5 Coatings comprising polyureas are of interest particularly in view of the facts that the reaction of polyisocyanates with amines proceeds extraordinarily quickly and the coated surfaces are very quickly serviceable (again). Furthermore, the presence of urea groups in polyurethanes results in a very favourable tradeoff between hardness and elasticity, and in many coating applications this is highly desirable.

10 Polyureas which can be used to coat pipes are described for example in EP-A 0 936 235. They are obtained by mixing a liquid aliphatic polyisocyanate, which in addition may also comprise a liquid epoxy resin, with a liquid aromatic polyamine. These coatings, though, are very brittle.

15 In order to make such polyurea coatings flexible it is possible to admix the aromatic diamines of EP-A 1 486 522 with, for example, polyhydroxy compounds such as polyether polyols or polyester polyols, prepolymers of hexamethylene diisocyanate (HDI), and also of its dimer and trimer, or else amine-terminated polyethers. These options for flexibilizing polyurea coatings have the following disadvantages, however: when polyethers and polyesters are employed, there is a considerable increase in the cure time, since the
20 NCO/OH reaction is markedly slower than the NCO/NH₂ reaction. Furthermore, polyesters have a high viscosity, which considerably hampers their processing in these highly reactive mixtures. Even simple prepolymers of HDI or its oligomers display excessive viscosity and, furthermore, incompatibilities in the fully reacted polyurea (inhomogeneous coatings). Since the reactivity of amine-terminated polyethers and aromatic diamines is very different, the
25 result, here as well, is inhomogeneous systems.

It was an object of the present invention, therefore, to provide compositions which exhibit low viscosity and can be cured under ambient conditions in a short time to form homogeneous, flexibilized polyureas.

30 Surprisingly it has now been found that compositions which contain particular (cyclo)aliphatic polyisocyanate prepolymers containing allophanate groups in combination

with polyamines and also optionally further polyisocyanates can be cured under ambient conditions in a short time to form homogeneous, flexible polyureas.

The invention provides compositions comprising

- 5 A) a polyisocyanate prepolymer which has polyether groups attached via allophanate groups, and
- B) polyamines containing at least two primary amino groups, and also
- C) optionally further polyisocyanates.

The allophanates employed in component A) are obtainable by reacting

- 10 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 the addition of

- A3) polyisocyanates, which may be different from those from A1), and
- A4) catalysts and
- 15 A5) optionally stabilizers.

Examples of suitable aliphatic and cycloaliphatic polyisocyanates A1) are di- or triisocyanates such as butane diisocyanate, pentane diisocyanate, hexane diisocyanate (hexamethylene diisocyanate, HDI), 4-isocyanatomethyl-1,8-octane 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_6XDI).
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In components A1) and A3) it is preferred to employ hexane diisocyanate (hexamethylene diisocyanate, HDI), 4,4'-methylenebis(cyclohexyl isocyanate) and/or 3,5,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane (isophorone diisocyanate, IPDI) as poly-
25 isocyanates. One very particularly preferred polyisocyanate is HDI.

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

As polyhydroxy compounds of component A2) it is possible to employ all of the polyhydroxy compounds known to the skilled person, which preferably have an average OH functionality of greater than or equal to 1.5, it being necessary for at least one of the
30 compounds included in A2) to be a polyether polyol.

Suitable polyhydroxy compounds which can be employed 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 employ, as
5 polyhydroxy compounds, exclusively substances of the aforementioned kind based on polyether.

The polyether polyols employed in A2) preferably have number-average molecular weights M_n of 300 to 20 000 g/mol, with particular preference 1000 to 12 000, with very particular preference 2000 to 6000 g/mol. They further possess preferably an average OH functionality
10 of ≥ 1.5 , with particular preference ≥ 1.90 , with particular preference ≥ 1.95 .

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

Particularly suitable polyether polyols of component A2) are those of the aforementioned
15 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).

Suitable starter molecules for the preparation of polyether polyols are, for example, simple polyols of low molecular weight, water, organic polyamines having at least two N-H bonds,
20 or any desired mixtures of starter molecules of these kinds. Alkylene oxides suitable for the alkoxylation are, in particular, ethylene oxide and/or propylene oxide, which can be employed in either order or else in a mixture in the alkoxylation.

Preferred starter molecules for preparing polyether polyols by alkoxylation, in particular by the DMC method, are, in particular, simple polyols such as ethylene glycol, propylene 1,3-
25 glycol and butane-1,4-diol, hexane-1,6-diol, neopentyl glycol, 2-ethylhexan-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 mass products of ethoxylation or propoxylation of simple polyols of this kind, or any desired mixtures of modified or non-modified alcohols of this kind.

The polyurethane prepolymers containing isocyanate groups are prepared by reacting the
30 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 110°C, optionally with the use of catalysts known per se from polyurethane chemistry, such as, for example, tin soaps, dibutyltin dilaurate or tertiary amines, e.g. triethylamine or diazabicyclooctane. The allophanatization then takes place subsequently by reaction of the resultant polyurethane prepolymers containing isocyanate groups with polyisocyanates A3), which may be the same as or different from those of component A1), suitable catalysts A4) for the allophanatization being added. Typically then acidic additives of component A5) are added additionally, for the purpose of stabilization, and excess polyisocyanate is removed from the product by means, for example, of thin-film distillation or extraction.

10 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.

For allophanatization it is preferred in A4) to employ zinc(II) compounds as catalysts, 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 Zn(II) bis(2-ethylhexanoate), Zn(II) bis(n-octate), Zn(II) bis(stearate) or mixtures thereof. These allophanatization catalysts are employed typically in amounts of up to 5% by weight, based on the reaction mixture as a whole. It is preferred to employ 5 to 500 ppm of the catalyst, with particular preference 20 to 200 ppm.

Optionally it is also possible, before, during or after the allophanatization, to use additives A5) which have a stabilizing action. These may be acidic additives such as Lewis acids (electron deficiency compounds) or Brönsted acids (protic acids) or compounds which liberate such acids under 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 form the corresponding acids. Mention may be made here in 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 acidic additives may also be used to deactivate the allophanatization catalyst. They improve, furthermore, the stability of the allophanates prepared in accordance with the invention, during thermal exposure in the course of thin-film distillation or else after the preparation, during storage of the products, for example. The acidic additives are generally added in at least an amount such that the molar ratio of

the acidic centres of the acidic additive and of the catalyst is at least 1:1. Preferably, however, an excess of the acidic additive is added. 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.

- 5 Excess monomeric diisocyanate can be separated off if desired after the allophanatization has been concluded. Thin-film distillation is the method preferred for this purpose, and is carried out in general at temperatures of 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 preference less than 0.5% by weight (diisocyanate).
- 10 The overall process steps for preparing the polyisocyanate prepolymer containing allophanate groups can be carried out optionally in the presence of inert solvents. Inert solvents in this context are understood as those which do not 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)-
- 15 aliphatic hydrocarbon mixtures or any desired mixtures of solvents of this kind. Preferably, however, the reactions according to the invention are carried out solvent-free.

The components involved can be added both during the preparation of the prepolymers containing isocyanate groups and during allophanatization, in any order. Preference is given, however, to adding the polyether polyol A2) to the initial polyisocyanate charge of components A1) and A3), and to adding the allophanatization catalyst A4) finally.

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In one preferred embodiment of the invention the polyisocyanates of components A1) and A3) are introduced as an initial charge in an appropriate reaction vessel and this initial charge is heated, with stirring if desired, to 40 to 110°C. After the desired temperature has been reached, the polyhydroxy compounds of component A2) are then added with stirring

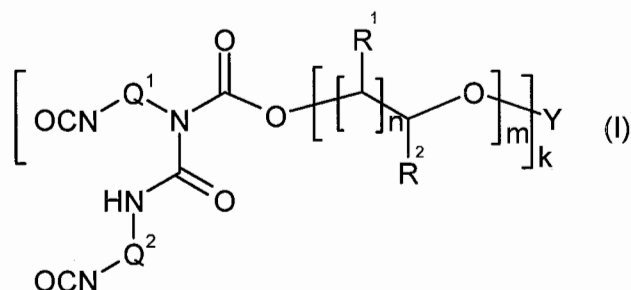
25 and stirring is continued until the NCO content matches or amounts to slightly below the theoretical NCO content of the polyurethane prepolymer anticipated in accordance with the chosen stoichiometry. At this point the allophanatization catalyst A4) is added and the reaction mixture is heated at 50 and 100°C until the NCO content matches or is slightly below the desired NCO content. Following addition of acidic additives as stabilizers A5),

30 the reaction mixture is cooled or passed on directly for thin-film distillation. In that procedure the excess polyisocyanate is separated off at temperatures from 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%. After the thin-film distillation it is possible to add any further stabilizer.

The allophanates thus obtainable for employment 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.

Furthermore, they 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 7500 mPas, with very particular preference from 1000 to 3500 mPas.

The allophanates as described above correspond typically to the general formula (I),



in which

10 Q^1 and Q^2 independently of one another stand for the radical of a linear and/or cyclic aliphatic diisocyanate of the type stated, preferably $-(\text{CH}_2)_6-$,

R^1 and R^2 independently of one another stand for hydrogen or a C_1 - C_4 alkyl radical, R^1 and R^2 being preferably hydrogen and/or methyl groups, it being possible for the definition of R^1 and R^2 to be different in each repeating unit m,

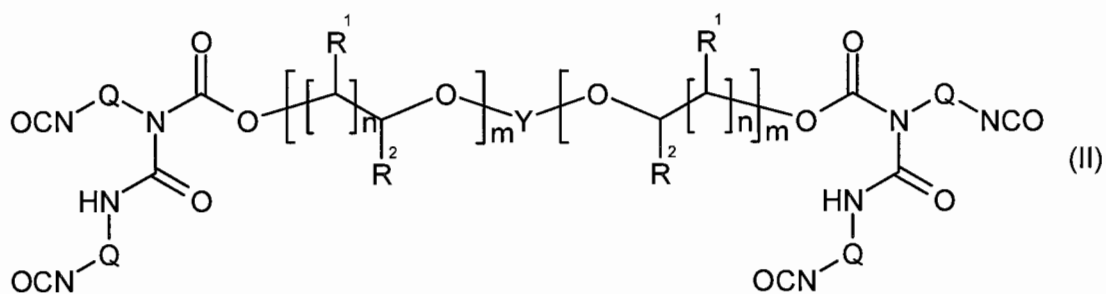
15 Y is the radical of a starter molecule of the stated kind, having a functionality of 2 to 6, and therefore

k stands for a value from 2 to 6, which, it will be appreciated, need also not be a whole number, owing to the use of different starter molecules, and also

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

n is 1 or 3.

It is preferred to obtain allophanates which correspond to the general formula (II),



in which

Q is the radical of a linear and/or cyclic aliphatic diisocyanate of the stated kind,
5 preferably $-(\text{CH}_2)_6-$,

R^1 and R^2 independently of one another stand for hydrogen or for a C_1 - C_4 alkyl radical, R^1
and R^2 being preferably hydrogen and/or methyl groups, it being possible for
the definition of R^1 and R^2 to be different in each repeating unit m,

Y stands for the radical of a difunctional starter molecule of the stated kind, and

10 m corresponds to sufficient monomer units that the number-average molecular
weight of the polyether on which the structure is based is 300 to 20 000 g/mol,
and

n is 1 or 3.

15 Since the allophanates of the formula (I) and (II) are generally prepared using polyols based
on polymerized ethylene oxide, propylene oxide or tetrahydrofuran, in the formulae (I) and
(II), in the case of $m = 1$ with particular preference at least one radical of R^1 and R^2 is
hydrogen, and in the case of $m = 3$ R^1 and R^2 are hydrogen.

Suitable polyamines B) are all aromatic, aliphatic, cycloaliphatic or heterocyclic, preferably
aromatic, compounds having at least two primary or secondary, preferably at least two
20 primary, amino groups per molecule.

Particularly suitable polyamines are aromatic diamines, examples being optimally substituted
tolylenediamines or methylenebis(anilines). Specific examples include diethyl-
tolylenediamines, dimethylthiotolylenediamines, particularly isomers thereof containing
amino groups in 2,4 and 2,6 position, and also mixtures thereof, 4,4'-methylenebis(2-
25 isopropyl-6-methylaniline), 4,4'-methylenebis(2,6-diisopropylaniline), 4,4'-methylenebis(2-
ethyl-6-methylaniline) and 4,4'-methylenebis(3-chloro-2,6-diethylaniline).

As further polyisocyanates C) it is possible in principle to use all conventional derivatives of aliphatic or cycloaliphatic polyisocyanates having a uretdione, biuret and/or isocyanurate structure which can be obtained by modifying conventional monomeric diisocyanates such as butane diisocyanate, pentane diisocyanate, hexane diisocyanate (hexamethylene diisocyanate, HDI), 4-isocyanatomethyl-1,8-octane diisocyanate (triisocyanatononane, TIN) or cyclic systems, such as 4,4'-methylenebis(cyclohexylisocyanate), 3,5,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane (isophorone diisocyanate, IPDI) and ω,ω' -diisocyanato-1,3-dimethylcyclohexane (H_6XDI).

Preferably the compositions of the invention comprise polyisocyanates C) having a uretdione structure, with particular preference uretdiones based on hexamethylene diisocyanate (HDI).

It will be appreciated that the typical auxiliaries and additives can be added to the compositions of the invention, such as pigments, (coatings) additives, thixotropic agents, flow control agents, emulsifiers and stabilizers.

The addition of catalysts for curing is typically not necessary though possible in principle.

Compositions of the invention are prepared by mixing components A), B) and optionally C) in any order before or during the application, as a coating for example. If a component C) is employed then it is preferably mixed first with component A) and then the resulting mixture is cured with component B).

The compositions of the invention can be applied to surfaces with the conventional techniques such as spraying, dipping, flooding or pouring. Following flashing off to remove any solvents present, the compositions being preferably free from solvents, the coatings then cure under ambient conditions, in particular at -20°C to $+40^{\circ}\text{C}$, or else at higher temperatures of $+40$ to $+200^{\circ}\text{C}$, for example.

The compositions specified can be applied for example to metals such as iron, steel, aluminium, bronze, brass, copper, plastics, ceramic materials such as glass, concrete, stone and natural substances, it being possible for the substrates stated to have been subjected to any required pretreatment beforehand. The compositions are applied preferably to iron or steel. On the basis of their rapid curing, the compositions of the invention are particularly suitable not least for the (interior) coating of pipes, especially pipes for conveying mineral oil, (drinking) water, gas or chemicals.

Examples

Unless otherwise indicated all percentages are by weight.

The NCO contents were determined by back-titrating dibutylamine added in excess with hydrochloric acid.

- 5 The viscosity measurement took place using a rotational viscometer from Haake at 23°C.

The extension and the tensile strength were determined in a tensile test in accordance with EN ISO 527. The Shore hardness was determined using a manual instrument from Erichsen.

- 10 Desmodur N 3400 (Bayer MaterialScience AG, Leverkusen, DE) is a polyisocyanate which is based on hexamethylene diisocyanate, contains uretdione groups and has an NCO content of 21.8%.

Ethacure 300 (Albemarle Corporation) is an isomer mixture composed of 3,5-dimethylthiotolylene-2,4-diamine and 3,5-dimethylthiotolylene-2,6-diamine and has an isocyanate equivalent weight of 107 g.

BYK A 530 is an additive available from Byk Chemie, Wesel, DE.

- 15 **Inventive Example 1:**

a) Preparation of a polyisocyanate containing allophanate groups:

- 20 First 90 mg of isophthaloyl dichloride were added to 2520.7 g of hexane 1,6-diisocyanate, after which the mixture was heated to 100°C with stirring. Then 1978.5 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 mg KOH/g, theoretical functionality 2) were added over the course of 3 hours. The reaction mixture was subsequently heated at 100°C until an NCO content of 26.1% was reached. Then the temperature was reduced 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%. Following
- 25 the addition of 360 mg of isophthaloyl dichloride the excess hexane 1,6-diisocyanate was removed by means of thin-film distillation at < 1 mbar and 140°C. The product thus obtained had the following characteristics:

NCO content:	5.81%
Viscosity (23°C):	2200 mPas

b) Preparation of a composition from the polyisocyanate containing allophanate groups from a) and an aromatic diamine:

100 parts by weight of the polymer prepared according to a) were mixed with 13.5 parts by weight of Ethacure 300 and the mixture was poured to give a film 2 mm thick. After curing (20 h at 40°C, then 3 d at room temperature) a transparent, homogeneous plastic was obtained which had the following mechanical data:

Extension: 46 %
Tensile strength: 48 MPa
Shore D hardness: 25

10 **Inventive Example 2:**

Starting from an allophanate prepared in the same way as for example 1a), compositions comprising a further polyisocyanate and an aromatic diamine were formulated, cured and subsequently tested.

15 The components indicated in the table below were added with stirring in the amount likewise indicated in the table, and within the potlife of approximately 25 minutes were poured out to give a film 2 mm thick. After curing (7 days at room temperature), transparent, homogeneous plastics were obtained, whose mechanical properties were subsequently measured (see table).

Table

	Composition 1 Amount [g]	Composition 2 Amount [g]
Allophanate from Ex. 1a)	290.5	219.0
Desmodur® N 3400	124.5	146.0
Ethacure® 300	107.0	107.0
Byk A 530	5.22	4.72
Extension [%]	95	90
Tensile strength [MPa]	19.5	22
Shore D hardness	52	64Ab

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Comparative Example 1:

a) Preparation of a polyisocyanate without allophanate groups:

734.7 g of hexane 1,6-diisocyanate were admixed over 5 h, heated with stirring at 100°C, with 865.0 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 mg KOH/g, theoretical functionality 2). The reaction mixture was subsequently heated at 100°C until an NCO content of 20.4% was reached. Following the addition of 320 mg of dibutyl phosphate the excess hexane 1,6-diisocyanate was removed by means of thin-film distillation at < 1 mbar and 140°C. The product thus obtained had the following characteristics:

10	NCO content:	3.21%
	Viscosity (23°C):	1360 mPas

b) Preparation of a composition from the polyisocyanate without allophanate groups from a) and an aromatic diamine:

15 54.3 parts by weight of the prepolymer prepared according to a) of comparative example 1 were mixed with 4.3 parts by weight of Ethacure 300 and the mixture was poured to give a film 2 mm thick. After curing (20 h at 40°C, then 3 d at room temperature), a transparent, homogeneous plastic was obtained. It was not possible to determine the Shore D hardness, since the test specimen was much too soft.

20 c) Preparation of a composition from the polyisocyanate without allophanate groups from a), a further polyisocyanate and an aromatic diamine:

25 30 parts by weight of the prepolymer prepared according to a) of comparative example 1 were mixed with 20 parts by weight of Desmodur N 3400 and 12.9 parts by weight of Ethacure 300 and the mixture was poured to give a film 2 mm thick. After curing (20 h at 40°C, 3 d at room temperature), a completely non-transparent, inhomogeneous plastic was obtained.

Aside from the inhomogeneity of the plastic, a Shore D hardness of only 38 was attained, in other words significantly less than for the comparable composition 2 of inventive example 2 (the weight ratio of the particular polyisocyanate employed to Desmodur N 3400 was in both cases 6:4).

30 **Comparative Example 2:**

30 g of an allophanate prepared from a low molecular weight monoalcohol and HDI, having an NCO content of 19.7% and a viscosity of 415 mPas, were mixed with 14.3 g of Ethacure 300 (1 minute's stirring) and the mixture was then poured out to form a plate 3 mm thick. After 2 h at room temperature and 20 h at 40°C, a plastic was obtained which, owing to its
5 high brittleness, could not be analysed for extension or tensile strength.

Claims

1. Compositions comprising
 - A) a polyisocyanate prepolymer which has polyether groups attached via allophanate groups, and
 - 5 B) polyamines containing at least two primary amino groups, and also
 - C) optionally further polyisocyanates.
2. Compositions according to Claim 1, characterized in that the allophanates employed in A) are prepared by reacting
 - A1) one or more aliphatic and/or cycloaliphatic polyisocyanates with
 - 10 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 the addition of
 - A3) polyisocyanates, which may be different from those from A1), and
 - 15 A4) catalysts
 - A5) optionally stabilizers.
3. Compositions according to Claim 2, characterized in that in the preparation of the allophanates employed in A) hexane diisocyanate (hexamethylene diisocyanate, HDI), 4,4'-methylenebis(cyclohexyl isocyanate) and/or 3,5,5-trimethyl-1-isocyanato-20 3-isocyanatomethylcyclohexane (isophorone diisocyanate, IPDI) are used as polyisocyanates in components A1) and A3).
4. Compositions according to Claim 2 or 3, characterized in that polyisocyanates of the same type are employed in A1) and A3).
5. Compositions according to any one of Claims 2 to 4, characterized in that zinc(II) 25 compounds are used as catalysts for allophanatization in A4).
6. Compositions according to Claim 5, characterized in that zinc(II) compounds used are zinc(II) bis(2-ethylhexanoate), Zn(II) bis(n-octoate), Zn(II) bis(stearate) or mixtures thereof.

7. Compositions according to any one of Claims 2 to 6, characterized in that polyether polyols are employed 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.
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8. Compositions 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. Compositions according to any one of Claims 2 to 8, characterized in that organic or inorganic acids, acid halides or esters are employed as stabilizers in A5).
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10. Compositions according to any one of claims 1 to 9, characterized in that aromatic diamines containing primary amino groups are employed in B).
11. Coatings obtainable from two-component coating systems according to any one of Claims 1 to 10.
12. Substrates coated with coatings according to Claim 11.
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