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(54) Titre : COMPOSITIONS DE REVETEMENT EN POUDRE POUVANT ETRE DURCIES SOUS RAYONNEMENT ET
LEUR UTILISATION

(54) Title: RADIATION CURABLE POWDER COATING COMPOSITIONS AND THEIR USE

(57) **Abrégé/Abstract:**

Disclosed is a radiation curable powder coating composition which crosslinks to lightfast and weather-stable film. The composition comprises (1) a binder compound of 60-90% by weight of at least one amorphous urethane acrylate and 10-40% by weight of at least one crystalline urethane acrylate, and (2) optionally, conventional auxiliaries and additives.



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Abstract:

Disclosed is a radiation curable powder coating composition which crosslinks to lightfast and weather-stable film. The composition comprises (1) a binder
5 compound of 60-90% by weight of at least one amorphous urethane acrylate and 10-40% by weight of at least one crystalline urethane acrylate, and (2) optionally, conventional auxiliaries and additives.

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Radiation curable powder coating compositions and their use

The invention relates to radiation curable powder coating compositions which crosslink to lightfast and weather-stable films.

5 Thermally crosslinkable powder coating materials are known and are much used in the paint processing industry.

For example, German Patent (DE-C) 27 35 497 describes polyurethane (PU) powder coatings having
10 outstanding weathering stability and heat stability. The crosslinkers whose preparation is described in DE-C 27 12 931 are composed of ϵ -caprolactam-blocked isophorone diisocyanate containing isocyanurate groups. Also known are
polyisocyanates containing urethane, biuret or urea groups,
15 their isocyanate groups again being blocked.

The disadvantage of these systems lies in the elimination of blocking agent during the thermal crosslinking reaction. Since, consequently, the blocking agent may be emitted into the environment, it is necessary on ecological
20 and industrial hygiene grounds to take special precautions to clean the outgoing air and/or to recover the blocking agent. Moreover, the reactivity of the crosslinkers is low. Curing temperatures above 170°C are required.

Both disadvantages - emission of blocking agent
25 and curing at high temperatures - can be removed by means of powder coating materials which are cured not thermally but instead by means of radiation. Radiation curable powder coating materials of this kind are known and are described in, for example, U.S. Patent No. 3,485,732, EP 0407826,
30 EP 0636669, WO 99/14254, U.S. Patent No. 3,974,303, U.S. Patent No. 5,639,560 and EP 0934359. EP 0636669 and

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WO 99/14254 describe two-component, radiation curable powder coating materials based on unsaturated polyesters and vinyl ethers. The coatings produced from them are unsuitable for outdoor use on account of their severe yellowing.

5 U.S. Patent No. 3,974,303 describes thermoplastic resins containing from 0.5 to 3.5 polymerizable unsaturated groups per 1,000 g molecular weight. The polyurethanes described (see Example 1), however, are not weather-stable and are of poor flexibility owing to the absence of
10 polyester groups and the low chain length.

U.S. Patent No. 5,639,560 describes radiation curable powder compositions comprising special crystalline polyesters, additionally containing methacrylic end groups, as binders. These powder compositions optionally comprise
15 ethylenically unsaturated oligomers, including urethane acrylates, in minor amounts, preferably up to 10 percent by weight. The radiation curable powder coating formulations presented in this patent, however, have significant disadvantages. They can be ground only at minus 80°C and,
20 in general, the resultant coatings are either not stable to outdoor weathering or not flexible. A particularly serious disadvantage is the very low pendulum hardness (according to König) of below 120 s.

EP 0934359 describes powder radiation curable
25 mixtures of amorphous and crystalline polyesters containing terminal methacrylate groups. The powder coatings produced from them do possess a higher glass transition temperature than the crystalline methacrylates of U.S. Patent No. 5,639,560. However, cooling is still required for their
30 grinding. Moreover, the hardness and adhesion of coatings are no more than satisfactory.

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It is an object of the present invention to provide radiation curable powder coating compositions which are stable on storage at 35°C and which also, after curing of the films, lead to coatings combining hardness with flexibility and stability to outdoor weathering. It ought to be possible to formulate these coatings both for high transparency and for opacity. Moreover, the powder coating materials ought to be able to be ground with little or no refrigerant.

10 Surprisingly it has been found that this object can be achieved by means of a radiation curable powder coating composition comprising as binder a mixture of at least one amorphous urethane acrylate and at least one crystalline urethane acrylate, the mixture having a glass transition point (Tg) of at least 35°C.

The invention provides a radiation-curable powder coating composition comprising:

I. a binder composed of a mixture of:

20 A) 60-90% by weight of at least one amorphous urethane acrylate and

B) 10-40% by weight of at least one crystalline urethane acrylate, the Tg of the mixture of A and B being at least 35°C; and

II. optionally auxiliaries and additives,

25 excluding UV initiators.

The invention further provides for the use of compositions comprising:

I. a binder composed of

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A) 60-90% by weight of at least one amorphous urethane acrylate and

B) 10-40% by weight of at least one crystalline urethane acrylate, the Tg of the mixture of A and B being at
5 least 35°C; and

II. optionally auxiliaries and additives,

excluding UV initiators for producing radiation curable powder coating compositions.

The invention likewise provides a process for
10 producing radiation curable powder coating compositions comprising:

I. a binder composed of

C) 60-90% by weight of at least one amorphous urethane acrylate and

15 D) 10-40% by weight of at least one crystalline urethane acrylate, the Tg of the mixture of A and B being at least 35°C; and

II. optionally auxiliaries and additives,

20 excluding UV initiators, by mixing the ingredients, while observing an upper temperature limit of between 120°C and 130°C, in heatable kneading devices, particularly extruders.

The invention also provides a process for producing coatings of high or low transparency by using
25 radiation curable powder coating compositions comprising:

I. a binder composed of

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A) 60-90% by weight of at least one amorphous urethane acrylate and

B) 10-40% by weight of at least one crystalline urethane acrylate, the Tg of the mixture of A and B being at least 35°C; and

II. optionally auxiliaries and additives, excluding UV initiators.

Urethane acrylates for the purposes of this invention are composed of a hydroxyl-containing polyester to which urethane groups and acrylate groups are attached by reaction with polyisocyanates and acrylate-containing alcohols.

A. The amorphous urethane acrylates of the invention are prepared from amorphous hydroxyl-containing polyesters (A1) having a Tg of 35-80°C by reaction with polyisocyanates (A2) and a compound containing both at least one alcohol group and at least one polymerizable acrylate group (A3). They contain both urethane groups and terminal acrylate groups.

A1. Amorphous hydroxyl-containing polyesters having a Tg of 35-80°C are prepared by polycondensation of appropriate dicarboxylic acids and diols. Condensation takes place conventionally in an inert gas atmosphere at temperatures from 100 to 260°C, preferably from 130 to 220°C, in the melt or in an azeotropic procedure, as described, for example, in Methoden der Organischen Chemie (Houben-Weyl), Volume 14/2, pages 1 to 5, 21 to 23, 40 to 44, Georg Thieme Verlag, Stuttgart, 1963, or in C.R. Martens, Alkyd Resins, pages 51 to 59, Reinhold Plastics Appl. Series, Reinhold Publishing Comp., New York,

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1961. The carboxylic acids preferred for preparing polyesters may be aliphatic, cycloaliphatic, aromatic and/or heterocyclic in nature and may if desired be substituted by halogen atoms and/or unsaturated. Examples thereof include the following: succinic, adipic, suberic, azelaic, sebacic, phthalic, terephthalic, isophthalic, trimellitic, pyromellitic, tetrahydrophthalic, hexahydrophthalic, hexahydroterephthalic, dichlorophthalic, tetrachlorophthalic, endomethylenetetrahydrophthalic, and glutaric acid, 1,4-cyclohexanedicarboxylic acid, and - where available - their anhydrides or esters. Particular suitability is possessed by isophthalic acid, terephthalic acid, hexahydroterephthalic acid, and 1,4-cyclohexanedicarboxylic acid.

Examples of suitable polyols include monoethylene glycol, 1,2- and 1,3-propylene glycol, 1,4- and 2,3-butylene glycol, di- β -hydroxyethylbutanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, decanediol, dodecanediol, neopentyl glycol, cyclohexanediol, 3(4),8(9)-bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane (digidol), 1,4-bis(hydroxymethyl)cyclohexane, 2,2-bis(4-hydroxycyclohexyl)propane, 2,2-bis[4-(β -hydroxyethoxy)phenyl]propane, 2-methylpropane-1,3-diol, 2-methylpentane-1,5-diol, 2,2,4(2,4,4)-trimethylhexane-1,6-diol, glycerol, trimethylolpropane, trimethylolethane, hexane-1,2,6-triol, butane-1,2,4-triol, tris(β -hydroxyethyl)isocyanurate, pentaerythritol, mannitol, and sorbitol, and also diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, polypropylene glycols, polybutylene glycols, xylylene glycol, and neopentyl glycol hydroxypivalate. Preference is given to monoethylene glycol, neopentyl glycol, digidol, cyclohexanedimethanol, trimethylolpropane, and glycerol.

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Amorphous polyesters thus prepared preferably have an OH number of 15-150 mg KOH/g, a Tg of 35-80°C, and an acid number of less than 5 mg KOH/g. It is also possible to use mixtures of amorphous polyesters.

5 A2. As polyisocyanates in the amorphous urethane acrylates of the invention use may be made of diisocyanates of aliphatic, (cyclo)aliphatic or cycloaliphatic structure. Representative examples of the polyisocyanates are 2-methylpentamethylene 1,5-diisocyanate, hexamethylene
10 diisocyanate, trimethylhexamethylene 1,6-diisocyanate, especially the 2,2,4- and 2,4,4- isomer and technical-grade mixtures of both isomers, 4,4'-methylenebis(cyclohexyl isocyanate), norbornane diisocyanate, and 3,3,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane (IPDI). Likewise
15 highly suitable in addition are polyisocyanates obtainable by reacting polyisocyanates with themselves by way of isocyanate groups, such as isocyanurates, formed by reaction of three isocyanate groups. The polyisocyanates may likewise contain biuret or allophanate groups. IPDI is
20 especially suitable.

A3. Suitable polymerizable compounds containing at least one free OH group and one polymerizable acrylate group include, for example, hydroxyethyl acrylate (HEA), hydroxypropyl acrylate, and glycerol diacrylate.
25 Hydroxyethyl acrylate (HEA) is especially suitable.

The preparation of the amorphous urethane acrylate A from the amorphous OH-containing polyesters A1, polyisocyanates A2, and the compounds A3 is generally well known. For example, the polyisocyanate is introduced as an
30 initial charge, DBTL as catalyst and IONOL*CP (Shell) as polymerization inhibitor are added, and the polyester is

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added in an NCO:OH ratio of 2.5-1.5:1. After the end of the addition, the reaction is completed at 100-140°C.

Thereafter, component A3, e.g., hydroxyethyl acrylate, in a residual-NCO:OH ratio of 1.0-1.1:1 is added to the reaction product and the reaction is completed at 80-140°C so as to give an NCO content of less than 0.1%. Also possible is a prior reaction of a polyisocyanate, e.g. IPDI, with component A3 and the addition of this NCO-containing precursor to the hydroxyl-containing polyester.

10 B. The crystalline urethane acrylates of the invention are prepared by reacting crystalline hydroxyl-containing polyesters (B1) with polyisocyanates (B2) and a component A3. Especially suitable as A3 is hydroxyethyl acrylate (HEA). They contain both urethane groups and
15 terminal acrylate groups.

B1. Crystalline hydroxyl-containing polyesters are prepared by polycondensation as already described for amorphous polyesters under A1. For this purpose an acid component, composed of 80-100 mol percent of a saturated
20 linear aliphatic or cycloaliphatic dicarboxylic acid having 4-14 carbon atoms and 0-20 mol percent of another aliphatic or cycloaliphatic or aromatic dicarboxylic or polycarboxylic acid is reacted with an alcohol component composed of 80-100 mol percent of a linear aliphatic diol having 2-15 carbon
25 atoms and 0-20% of another aliphatic or cycloaliphatic diol or polyol having 2-15 carbon atoms. The crystalline hydroxyl-containing polyesters thus prepared have an OH number of 15-150 mg KOH/g, an acid number < 5 mg KOH/g and a melting point of 40-130°C.

30 Preferred carboxylic acids for preparing crystalline polyesters are succinic, adipic, suberic,

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azelaic, sebacic, dodecanedioic, tetrahydrophthalic, hexahydrophthalic, hexahydroterephthalic, endomethylenetetrahydrophthalic, isophthalic, terephthalic, 1,4-cyclohexanedicarboxylic, and glutaric acids, and - where
5 available - their anhydrides or esters. Especially suitable are succinic acid, adipic acid, sebacic acid and dodecanedioic acid.

Suitable polyols include the following diols:
ethylene glycol, propane-1,2-diol and propane-1,3-diol,
10 2,2-dimethylpropane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 2-methylpentane-1,5-diol, 2,2,4-trimethylhexane-1,6-diol, 2,4,4-trimethylhexane-1,6-diol, heptane-1,7-diol, decane-1,10-diol, dodecane-1,12-diol, 9,10-octadecene-1,12-diol, octadecane-1,18-diol, 2,4-dimethyl-2-
15 propylheptane-1,3-diol, butene-1,4-diol, butyne-1,4-diol, diethylene glycol, triethylene glycol, tetraethylene glycol, trans- and cis-1,4-cyclohexanedimethanol; the triols glycerol, hexane-1,2,6-triol, 1,1,1-trimethylolpropane, and 1,1,1-trimethylolethane; and the tetraol pentaerythritol.

20 B2. For preparing the crystalline urethane acrylates of the invention it is preferred to use, as polyisocyanates, diisocyanates of aliphatic, (cyclo)aliphatic or cycloaliphatic structure. Representative examples of the polyisocyanates are 2-methylpentamethylene 1,5-diisocyanate, hexamethylene
25 diisocyanate, trimethylhexamethylene 1,6-diisocyanate, especially the 2,2,4- and 2,4,4- isomer and technical-grade mixtures of both isomers, 4,4'-methylenebis(cyclohexyl isocyanate), norbornane diisocyanate, and 3,3,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane (IPDI). Likewise
30 highly suitable in addition are polyisocyanates obtainable by reacting polyisocyanates with themselves by way of isocyanate groups, such as isocyanurates, formed by reaction of three

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isocyanate groups. The polyisocyanates may likewise contain biuret or allophanate groups. IPDI is especially suitable.

B3. The polymerizable compounds are identical with component A3.

5 The preparation of the urethane acrylates B of the invention from crystalline OH-containing polyesters B1, polyisocyanates B2, and B3 is generally well known. For instance, the polyisocyanate is introduced as an initial charge, DBTL as catalyst and IONOL*CP (Shell) as
10 polymerization inhibitor are added, and the polyester is added in an NCO:OH ratio of 2.5-1.5:1. After the end of the addition, the reaction is completed at 70-130°C. Thereafter, component B3, e.g., hydroxyethyl acrylate, in a residual-NCO:OH ratio of 1.0-1.1:1 is added to the reaction
15 product and the reaction is completed at 70-130°C so as to give an NCO content of less than 0.1%.

Amorphous and crystalline urethane acrylates are mixed in a weight ratio of amorphous to crystalline of 60:40 to 90:10, so that the end

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product has a Tg of at least 35°C. It is also possible to mix the amorphous and crystalline starting polyesters and then to react the mixture with polyisocyanates and acrylate-containing alcohols.

- 5 For the radiation curing of the powder coating composition of the invention, accelerated electron beams are suitable. The electron beams generate free radicals from the powder coating composition, in a number which ensures extremely rapid polymerization of the reactive acrylate groups. It is preferred to use radiation doses of from 5 to 15 Mrad.
- 10 The use of initiators, e.g., thioxanthenes, phosphine oxides, metallocenes, tertiary aminobenzenes or tertiary aminobenzophenones, which break down into free radicals on exposure to visible light is likewise possible.
- 15 Optional additives are acrylate or methacrylate compounds, such as the triacrylate of tris(2-hydroxyethyl) isocyanurate (SR 386, Sartomer^{*}), and adhesion promoters, which may be used in minor fractions of 0-20% by weight in order to modify the coating properties.
- 20 Further additives customary in the case of powder coating materials are leveling agents, light stabilizers, and devolatilizers. These may be used at 0-5% by weight. Also possible is the use of pigments and extenders, e.g., metal oxides such as titanium dioxide and metal hydroxides, sulfates, sulfides, carbonates, silicates, talc, carbon black, etc., in weight fractions of
- 25 0-30%.

In order to prepare the ready-to-use powder coating composition the ingredients are mixed. Homogenization of the ingredients may take place in suitable apparatus, such as heatable kneading devices, for example, but

30 preferably by extrusion, with recommended upper temperature limits of 120-130°C. Following cooling to room temperature and appropriate size reduction, the extrudate is ground to the ready-to-spray powder without addition of refrigerants. Application of the ready-to-spray powder to appropriate substrates may take place in accordance with the known

35 methods, such as by electrostatic or tribostatic powder spraying, fluidized bed sintering or electrostatic fluid-bed sintering, for example. Examples of suitable substrates include untreated and pretreated metallic substrates, wood, wood materials, plastics, glass, and paper.

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The coatings produced from the powder coating compositions of the invention may be formulated to range from highly transparent to opaque.

- 5 The invention accordingly further provides for the use of the radiation curable powder coating compositions for producing coatings having high or low transparency.

The invention is illustrated by the following examples:

10

Examples:

1. General preparation procedure for hydroxyl-containing polyesters

15

Acid components and alcohol components are admixed with 0.2 percent by mass of n-butyltin trioctanoate and heated at 190°C under nitrogen and with stirring in an apparatus provided with a distillation column. As water is separated out, this temperature is slowly raised to 230°C. After about 98% of the theoretical amount of water has been removed by distillation, the product is cooled and tested for OH number (OHN in mg KOH/g) and acid number (AN in mg KOH/g).

20

In this way, four polyesters are prepared:

25

A1: amorphous polyester composed of IPA 100%, MEG 20% and NPG 80%, OHN 42 mg KOH/g, Tg 48°C

A2: amorphous polyester composed of IPA 100%, MEG 20% and DCD 80%, OHN 40 mg KOH/g, Tg 75°C

30

B1: crystalline polyester composed of DDA 100%, MEG 100%, OHN 31 mg KOH/g, m.p.: 81°C

B2: crystalline polyester composed of SSA 100%, 1,4-BD 100%, OHN 31 mg KOH/g, m.p.: 113°C

SSA: succinic anhydride, DDA: dodecanedioic acid, IPA: isophthalic acid,
35 1,4-BD: 1,4-butanediol, MEG: monoethylene glycol, NPG: neopentyl glycol,
DCD: dicitol

2. Preparation of the amorphous urethane acrylate A1U

111.2 g of the polyester A1 (OHN 42) are melted and added in portions at 120°C with vigorous stirring to a mixture of 23.7 g of IPDI, 0.3 g of IONOL*CP and 0.3 g of DBTL. After 30 minutes of reaction, 14.9 g of hydroxyethyl acrylate are additionally added dropwise. After a further 30 minutes of stirring, the NCO content is below 0.1% and the hot reaction mixture is poured from the flask onto a sheet. As soon as the reaction mass has solidified and cooled, it is mechanically size-reduced and ground. The Tg of this product is 41°C.

10

3. Preparation of the amorphous urethane acrylate A2U

37.7 g of the polyester A2 (OHN 40) are melted and added in portions at 140°C with vigorous stirring to a mixture of 7.5 g of IPDI, 0.1 g of IONOL*CP and 0.1 g of DBTL. After 30 minutes of reaction, 4.7 g of hydroxyethyl acrylate are additionally added dropwise. After a further 30 minutes of stirring, the NCO content is below 0.1% and the hot reaction mixture is poured from the flask onto a sheet. As soon as the reaction mass has solidified and cooled, it is mechanically size-reduced and ground. The Tg of this product is 62°C.

15

20

4. Preparation of the crystalline urethane acrylate B1U

103.8 g of the polyester B1 (OHN 31) are melted and added in portions at 90°C with vigorous stirring to a mixture of 16.1 g of IPDI, 0.1 g of IONOL*CP and 0.1 g of DBTL. After 30 minutes of reaction, 10.1 g of hydroxyethyl acrylate are additionally added dropwise. After a further 30 minutes of stirring, the NCO content is below 0.1% and the hot reaction mixture is poured from the flask onto a sheet. As soon as the reaction mass has solidified and cooled, it is mechanically size-reduced and ground. The melting point of this product is 80°C.

25

30

5. Preparation of the crystalline urethane acrylate B2U

103.8 g of the polyester B2 (OHN 31) are melted and added in portions at 90°C with vigorous stirring to a mixture of 16.1 g of IPDI, 0.1 g of IONOL*CP and 0.1 g of DBTL. After 30 minutes of reaction, 10.1 g of hydroxyethyl acrylate are additionally added dropwise. After a further 30 minutes of stirring, the NCO content is below 0.1%

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and the hot reaction mixture is poured from the flask onto a sheet. As soon as the reaction mass has solidified and cooled, it is mechanically size-reduced and ground. The melting point of this product is 109°C.

5

6. Preparation of inventive polymers and powder coating compositions and of the comparative experiments

The three constituents A1U, A2U and BU are mixed in the appropriate weight ratio and 100 parts of this mixture are admixed with 0.5 part of BYK^{*} 361 (leveling agent, BYK Chemie), 0.5 part of benzoin (devolatilizer, Aldrich) and 1 part of EBECRYL^{*} 170 (adhesion promoter, UCB). The size-reduced ingredients are intimately mixed in an edge runner mill and then homogenized in an extruder at not more than 130°C. After cooling, the extrudate is fractionated and ground to a particle size < 100 µm using a pinned-disk mill, with (in the case of the comparative experiments) and without (in the case of the inventive example) the addition of refrigerants (liquid nitrogen or dry ice). The powder thus prepared is applied using an electrostatic powder spraying unit at 60 kV to degreased and optionally pretreated iron panels. It is then melted under IR irradiation and cured by means of electron beams (15 Mrad).

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For comparative example Z the following formulation was used:

25

300 g UVECOAT^{*} 2100 (UCB)

86 g UVECOAT^{*} 9010 (UCB)

8 g IRGACURE^{*} 184 (CIBA)

4 g RESIFLOW^{*} PV 5 (Worlée)

2 g WORLÉE^{*} Add 900 (Worlée)

30 The parameters are summarized in Table 1:

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Table 1

Experiment	A1U	A2U	B1U	B2U	Total T _g [°C]	Grindable without Refrig. ₁	HK ² [sec]	EC ³ [mm]	BI ⁴ [in *lb]	SS ⁵	Opacity ⁶ [%]
1	56	24	20	-	43	Yes	176	>10	80	>7d	82
2	56	24	-	20	45	Yes	194	>10	>80	>7d	12
Comp. X			100	100	-80	No	70	>10	>80	<1d	-
Comp. Y	80		20	20	32	No	135	10	>80	1d	-
Comp. Z						No	88	6.4	50		-

1: Grindability without use of refrigerant

2: Hardness according to König (DIN 53 157)

3: Erichsen cupping (DIN 53 156)

4: Ball impact, direct (DIN EN ISO 6272)

5: Storage stability at 35°C (test for blocking resistance of the powder)

6: Transparency at a wavelength of 500 nm

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Only the inventive experiments 1 and 2 are grindable without addition of refrigerant and, moreover, exhibit a combination of high hardness, flexibility, and storage stability in the coating. All noninventive, comparative examples (Comp. X, Y and Z) have deficiencies in at least one of these
5 respects. Additionally, using the powder coating compositions 1 and 2 of the invention it is possible to produce coatings having very different light transmittances.

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CLAIMS:

1. A radiation curable powder coating composition comprising a binder composed of:

5 A) 60-90% by weight of at least one amorphous urethane acrylate, and

B) 10-40% by weight of at least one crystalline urethane acrylate,

with the glass transition temperature of the mixture of A and B being at least 35°C.

10 2. The composition of claim 1, wherein the amorphous urethane acrylate A is synthesized by reacting:

A1) at least one amorphous hydroxyl-containing polyester having a glass transition temperature of 35-80°C;

A2) at least one polyisocyanate; and

15 A3) at least one compound containing at least one alcohol group and at least one polymerizable acrylate group.

3. The composition of claim 2, wherein the amorphous polyester A1 is prepared by polycondensation of at least one polyol and at least one monomeric dicarboxylic acid.

20 4. The composition of claim 3, wherein the dicarboxylic acid is aliphatic, cycloaliphatic, aromatic or heterocyclic.

5. The composition of claim 3 or 4, wherein the dicarboxylic acid is selected from the group consisting of
25 succinic, adipic, suberic, azelaic, sebacic, phthalic, terephthalic, isophthalic, trimellitic, pyromellitic, tetrahydrophthalic, hexahydrophthalic,

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hexahydroterephthalic, dichlorophthalic, tetrachlorophthalic, endomethylenetetrahydrophthalic, glutaric acid, 1,4-cyclohexanedicarboxylic acid, anhydrides thereof, and esters thereof.

5 6. The composition of claim 3, wherein the dicarboxylic acid is selected from the group consisting of isophthalic acid, terephthalic acid, hexahydroterephthalic acid, and 1,4-cyclohexanedicarboxylic acid.

7. The composition of any one of claims 3 to 6,
 10 wherein the polyol is selected from the group consisting of monoethylene glycol, 1,2- and 1,3-propylene glycol, 1,4- and 2,3-butylene glycol, di- β -hydroxyethylbutanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, decanediol, dodecanediol, neopentyl glycol, cyclohexanediol, 3(4),8(9)-
 15 bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane (digidol), 1,4-bis(hydroxymethyl)cyclohexane, 2,2-bis(4-hydroxycyclohexyl)propane, 2,2-bis[4-(β -hydroxyethoxy)phenyl]propane, 2-methylpropane-1,3-diol, 2-methylpentane-1,5-diol, 2,2,4(2,4,4)-trimethylhexane-1,6-
 20 diol, glycerol, trimethylolpropane, trimethylolethane, hexane-1,2,6-triol, butane-1,2,4-triol, tris(β -hydroxyethyl)isocyanurate, pentaerythritol, mannitol, sorbitol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, polypropylene glycols, polybutylene glycols, xylylene
 25 glycol, and neopentyl glycol hydroxypivalate.

8. The composition of any one of claims 3 to 6, wherein the polyol is selected from the group consisting of monoethylene glycol, neopentyl glycol, digidol, cyclohexanedimethanol, trimethylolpropane, and glycerol.

30 9. The composition of any one of claims 2 to 8, wherein the polyisocyanate A2 is selected from the group

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consisting of isocyanurate, aliphatic diisocyanate, (cyclo)aliphatic diisocyanate, and cycloaliphatic diisocyanate.

10. The composition of any one of claims 2 to 8,
5 wherein the polyisocyanate is selected from the group consisting of 2-methylpentamethylene 1,5-diisocyanate, hexamethylene diisocyanate, 4,4'-methylenebis(cyclohexyl isocyanate), norbornane diisocyanate, 2,2,4-trimethylhexamethylene, 2,4,4-trimethylhexamethylene,
10 3,3,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane, and mixtures thereof.

11. The composition of claim 10, wherein the polyisocyanate is 3,3,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane.

15 12. The composition of any one of claims 2 to 11, wherein the component A3 is selected from the group consisting of hydroxyethyl acrylate (HEA), hydroxypropyl acrylate, and glycerol diacrylate.

20 13. The composition of any one of claims 2 to 12, wherein hydroxyethyl acrylate is used as component A3.

14. The composition of any one of claims 1 to 13, wherein the crystalline urethane acrylate B is synthesized by reacting:

25 B1) at least one crystalline hydroxyl-containing polyester;

B2) at least one polyisocyanate; and

B3) at least one compound containing at least one alcohol group and at least one polymerizable acrylate group.

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15. The composition of claim 14, wherein the crystalline polyester B1 is prepared by polycondensation of:

a) an acid component composed of i) 80-100 mol % of a saturated linear aliphatic or cycloaliphatic dicarboxylic acid having 4-14 carbon atoms and ii) 0-20 mol % of another aliphatic, cycloaliphatic or aromatic polycarboxylic acid, with

b) an alcohol component composed of i) 80-100 mol % of a linear aliphatic diol having 2-15 carbon atoms and ii) 0-20 mol % of another aliphatic or cycloaliphatic polyol having 2-15 carbon atoms.

16. The composition of claim 15, wherein the acid component is selected from the group consisting of succinic, adipic, suberic, azelaic, sebacic, dodecanedioic, tetrahydrophthalic, hexahydrophthalic, hexahydroterephthalic, endomethylenetetrahydrophthalic, isophthalic, terephthalic, 1,4-cyclohexanedicarboxylic, glutaric acids, anhydrides thereof and esters thereof.

17. The composition of claim 15, wherein the acid component is selected from the group consisting of succinic acid, adipic acid, sebacic acid and dodecanedioic acid.

18. The composition of any one of claims 15 to 17, wherein the alcohol component is selected from the group consisting of ethylene glycol, propane-1,2-diol, propane-1,3-diol, 2,2-dimethylpropane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 2-methylpentane-1,5-diol, 2,2,4-trimethylhexane-1,6-diol, 2,4,4-trimethylhexane-1,6-diol, heptane-1,7-diol, decane-1,10-diol, dodecane-1,12-diol, 9,10-octadecene-1,12-diol, octadecane-1,18-diol, 2,4-dimethyl-2-propylheptane-1,3-diol, butene-1,4-diol, butyne-1,4-diol,

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diethylene glycol, triethylene glycol, tetraethylene glycol, trans- and cis-1,4-cyclohexanedimethanol, glycerol, hexane-1,2,6-triol, 1,1,1-trimethylolpropane, 1,1,1-trimethylolethane, and tetraol pentaerythritol.

5 19. The composition of any one of claims 14 to 18, wherein the polyisocyanate B2 is selected from the group consisting of isocyanurate, aliphatic diisocyanate, (cyclo)aliphatic diisocyanate, and cycloaliphatic diisocyanate.

10 20. The composition of any one of claims 14 to 18, wherein the polyisocyanate is selected from the group consisting of 2-methylpentamethylene 1,5-diisocyanate, hexamethylene diisocyanate, 4,4'-methylenebis(cyclohexyl isocyanate), norbornane diisocyanate,
15 2,2,4-trimethylhexamethylene, 2,4,4-trimethylhexamethylene, 3,3,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane, and mixtures thereof.

21. The composition of claim 20, wherein the polyisocyanate is 3,3,5-trimethyl-1-isocyanato-3-
20 isocyanatomethylcyclohexane.

22. The composition of any one of claims 14 to 21, wherein the component B3 is selected from the group consisting of hydroxyethyl acrylate (HEA), hydroxypropyl acrylate, and glycerol diacrylate.

25 23. The composition of any one of claims 14 to 22, wherein hydroxyethyl acrylate is used as component B3.

24. The composition of any one of claims 1 to 23, further comprising auxiliaries and additives, with the exclusion of UV additives.

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25. The composition of claim 24, wherein the auxiliaries and additives comprise leveling agents, light stabilizers, devolatilizers, pigments, fillers, adhesion promoters, acrylate-containing and methacrylate-containing compounds other than the amorphous and crystalline urethane acrylates used as the binder.
26. The composition of any one of claims 1 to 25, further comprising an initiator selected from the group consisting of thioxanthenes, phosphine oxides, metallocenes, tertiary aminobenzenes and tertiary aminobenzophenones.
27. A process for producing the radiation curable powder coating composition of any one of claims 1 to 23, which comprises mixing the amorphous and crystalline urethane acrylates A) and B) in an apparatus, while an upper temperature limit of between 120°C and 130°C is maintained.
28. The process of claim 27, wherein an extruder is used to maintain the upper temperature limit.
29. A process for producing a coating, which comprises:
- 20 applying the radiation curable powder coating composition of any one of claims 1 to 26 to a substrate, and
- curing the coating composition by irradiating accelerated electron beams.
30. A radiation curable powder coating composition
- 25 comprising:
- A) a binder composed of 75-85% by weight of a mixture of two amorphous urethane acrylates, and

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B) 15-25% by weight of a crystalline urethane acrylate,

with the mixture of A and B having a glass transition temperature in the range of 40-50°C, wherein:

5 the mixture of amorphous acrylates comprises:

a) 65-75% of an amorphous acrylate synthesized by reacting:

10 (i) an amorphous polyester composed of isophthalic acid and a mixture of 15-25% by weight of ethylene glycol and 75-85% by weight of neopentyl glycol, with

(ii) 3,3,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane, and

(iii) hydroxyl ethyl acrylate,

15 in the presence of a catalyst and a polymerization inhibitor; and

b) 25-35% of a second amorphous acrylate synthesized by reacting:

20 (i) an amorphous polyester composed of isophthalic acid and a mixture of 15-25% by weight of ethylene glycol and 75-85% by weight of dicitol, with

(ii) 3,3,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane, and

25 (iii) hydroxyl ethyl acrylate,

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in the presence of a catalyst and a polymerization inhibitor;

and the crystalline urethane acrylate is synthesized by reacting:

- 5 (i) a crystalline polyester composed of dodecanedioic acid and monoethylene glycol, with
- (ii) 3,3,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane, and
- (iii) hydroxyl ethyl acrylate,

10 in the presence of a catalyst and a polymerization inhibitor.

31. The composition of claim 30, wherein succinic anhydride and 1,4-butanediol are used in place of dodecanedioic acid and monoethylene glycol, respectively, in
15 the synthesis of the crystalline urethane acrylate.

32. The composition of claim 30 or 31, further comprising a leveling agent, devolatilizer and an adhesion promoter.

33. A process for producing a coating, which comprises:
20 applying the radiation curable powder coating composition of any one of claims 44 to 46 to a substrate, and
curing the coating composition by irradiating accelerated electron beams in a dose of 12-15 MRad.

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