A powder paint binder composition

Composition de liant pour peinture en poudre

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The file contains technical information submitted after the application was filed and not included in this specification.
Description

[0001] The invention relates to a powder paint binder composition, and more particularly to a binder composition comprising a hydroxyl functional polymer and a crosslinker containing blocked isocyanate groups.

[0002] Such binder compositions are described in WO 93/23447. The crosslinker containing blocked isocyanate groups has to be stored cool because the glass transition temperature (Tg) of the crosslinker is close to room temperature. This is a disadvantage in the preparation of a powder paint, which involves dry mixing of the various components (polymers, crosslinkers, pigments and other additives) in a premix, prior to final preparation of the paint in the extruder.

[0003] The object of the present invention is to provide a binder composition for powder paints wherein the binder composition comprises a hydroxyl functional polymer and a crosslinker containing blocked isocyanate groups and wherein the powder paint composition can be cured to a powder coating at a relatively low temperature (for instance between 130°C and 170°C and in 10 to 30 minutes). The binder composition should also result in powder paint compositions having a combination of desired properties and in a powder stable system, in which the powder paint particles do not tend to agglomerate.

[0004] The invention is characterized in that the crosslinker includes (i) a crystalline compound containing blocked isocyanate groups and (ii) an amorphous compound containing blocked isocyanate groups.

[0005] The binder composition according to the invention results in powder coatings meeting the above-described objectives and offering good flow, flexibility, outdoor durability and clearness. The powder paint composition can be cured at temperatures of for instance between 130°C and 170°C and in 10 to 30 minutes.

[0006] The binder composition according to the present invention contains blocked 1,6-hexamethylene diisocyanate trimer (HDT) (for instance Tolonate HD™ from Rhône Poulenc or Desmodur N3300™ from Bayer) as amorphous compound, and blocked 1,6-hexamethylene diisocyanate (HDI) (for instance Tolonate HDT™ from Rhône Poulenc) as (semi)crystalline compound. Preferably 1,2,4-triazole is the blocking agent.

[0007] The crosslinker obtained in this way is a mixture of an amorphous and a (semi)crystalline compound. Said mixture is a solid compound at room temperature (about 25°C) that can be handled very easily. Generally, the melting point of the product is between about 50°C and about 130°C, and preferably between about 90°C and about 125°C.

[0008] This crosslinker can be ground and pulverized in an excellent manner and can be used in combination with hydroxyl functional resins in clear as well as in pigmented systems.

[0009] The equivalent ratio with respect to equivalents of blocked isocyanate groups between the crystalline compound (i) and the amorphous compound (ii) is between 8:2 and 3:7 and is preferably between 7:3 and 6:4.

[0010] The hydroxyl functional polymer is preferably a polyester, a polyacrylate or a mixture of both.

[0011] Preferably the polyester has a hydroxyl number of between 20 and 100 mg of KOH/gram of resin and an acid number of less than 20 mg of KOH/gram of resin.

[0012] Preferably the polyacrylate has a hydroxyl number of between 40 and 150 mg of KOH/gram of resin and an acid number of less than 20 mg of KOH/gram of resin.

[0013] The curing reaction of isocyanates and hydroxyl compounds is described by Misev, Powder Coatings, Chemistry and Technology, pp. 56-68 (John Wiley, 1991). The preparation of powder paints and the curing reactions thereof to obtain powder coatings are generally described in said book at pp. 42-45.

[0014] The weight ratio between the polymer containing hydroxyl groups and the crosslinker can be between about 95:5 and about 50:50, and preferably, between 93:7 and 70:30. This ratio depends on, among other factors, the hydroxyl number of the polymer.

[0015] The hydroxyl functional polymers can be mixed with the blocked crosslinker by extrusion, for instance, at a temperature of about 100°C. The curing takes place at temperatures of, for instance, between about 130°C and about 170°C (in, for instance, about 10-40 minutes), and preferably below about 150°C.

[0016] Additives, such as for example fillers, catalysts, curing agents, flow agents and/or stabilizers and, if required, pigments, can be added to the coating systems, preferably before the extrusion.

[0017] Suitable polyesters can be obtained via customary preparation methods from carboxylic acids or equivalents thereof. Use of mainly aromatic carboxylic acids is preferred. Examples include phthalic acid, isophthalic acid, terephthalic acid, pyromellitic acid, trimellitic acid, 3,6-dichlorophthalic acid, tetrachlorophthalic acid, and in so far as available, equivalents like anhydrides, acid chlorides or lower alkyl esters thereof. Generally the carboxylic acid component comprises at least 50 wt.%, and preferably at least 70 mol% isophthalic acid and/or terephthalic acid.

[0018] Preferably the diol component of the polyester is an aliphatic diol. Examples include ethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,2-diol, butane-1,4-diol, butane-1,3-diol, 2,2-di-methylpropane diol-1,3 (= neopentyl glycol), hexane-1,6-diol, 2,2-[bis(2-hydroxyethoxy)]phenylpropane and smaller quantities of polyols, such as for example glycerol, hexane triol, pentaerytritol, sorbitol, trimethylol ethane, trimethylol propane and tris-(2-hydroxy)-isocyanurate, can be used as alcohols. It is also possible to use epoxy compounds instead of diols and polyols, respectively. The alcohol component preferably contains at least 50 mol% neopentylglycol.
The polymeric acrylic acid polymer is preferably prepared by a polymerization reaction, in which a solvent, such as toluene, xylene or butyl acetate, is supplied to a reactor. Then heating to the desired reaction temperature, such as for instance in the reflux temperature of the solvent, is effected. Then, for a period of for instance between 2 and 4 hours monomers, initiator and, optionally, mercaptan are added. Then the reaction temperature is kept at the reflux temperature for two hours for instance. Next, the solvent is distilled off by raising the temperature and subsequently a vacuum distillation is carried out, for instance over two hours for instance. The final product is drained and cooled.

According to a preferred embodiment of the invention, the hydroxyl functional acrylate resin is based on

- i) 8-30 wt.% hydroxyethyl acrylate,
- ii) 5-25 wt.% n-butyl methacrylate and
- iii) 50-80 wt.% methyl methacrylate (i+ii+iii = 100 wt.%).

Hydroxyl functional acrylate resins can be prepared in a polymerization reaction, in which a solvent, such as toluene, xylene or butyl acetate, is supplied to a reactor. Then heating to the desired reaction temperature, such as for instance the reflux temperature of the solvent is effected. Then, for a period of for instance between 2 and 4 hours monomers, initiator and, optionally, mercaptan are added. Then the temperature is kept at the reflux temperature for two hours for instance. Next, the solvent is distilled off by raising the temperature and subsequently a vacuum distillation is carried out, for one to two hours for instance. The final product is drained and cooled.

The powder paint formulations produced with the binder composition according to the invention can be used for instance on metal, plastic and wood.

The powder paint formulations according to the invention can be used for instance for powder coatings that are suitable for domestic appliances, for industrial applications and automotive applications such as topcoats.

The clear top coats that are used according to the state of the art in the automotive industry as a two-component system are solvent-containing paint systems on the basis of acrylate resins, and cured with isocyanates. In order to meet the requirements concerning reduction of solvents emission, so-called 'high solids' systems are already used. The only way to reduce the emission of solvents even further is to use powder coatings for the clear coat on cars (Lattke, E. 'Pulverlack am Auto aus der Sicht der Autoindustrie', presented at 'Der Pulvertreff '92', 23.01.92, Munich).

However, powder paint systems for automotive application will have to meet the same requirements as the solvent-containing systems. These requirements relate for instance to flow, chemical resistance, gloss and outdoor durability (Kinza, W. 'Pulverklarlack für die Karosseriebeschichtung', presented at 'Die EPS-Praxis 1991', 25.11.91, Bad Nauheim). The aim is to realize these properties at a curing temperature between for instance 140°C and 170°C. Among the current powder resin systems there are no systems known which possess the required combination of properties. Although a number of properties can be achieved with systems on the basis of an acid/epoxy curing reaction, the required combination of good flow, good chemical resistance, high gloss, high scratch resistance, good mechanical properties and good outdoor durability has never been obtained with powder coatings.

The coatings obtained can be applied on motorcar components such as wheels, wheel caps, doors and wings.
Thermosetting powder paint compositions for industrial coatings are described generally in Misev, Powder Coatings, Chemistry and Technology at pp. 131-173 and 224-228.

The invention will be elucidated by means of the following, non-restrictive experiments and examples.

**Examples**

**Preparation of an acrylate resin**

**Experiment 1**

1650 grammes of toluene was supplied to a 6-litre reactor vessel equipped with a thermometer, a stirrer and a reflux cooler. With stirring and while a nitrogen flow was passed through the reactor, the temperature was raised to reflux temperature. Initiator tert.butylperoxy-2-ethyl-hexanoate (Triganox 21S™; AKZO) was dissolved in the mixture of monomers in amounts given in Table 1, the total monomer quantity being 3300 grams. Next, this mixture was supplied to the reactor in 3 hours. The temperature in the reactor was kept at reflux temperature. Immediately after the monomer mixture had been supplied, an additionally quantity of initiator was added. Two hours after the monomers had been supplied a separation vessel was included in the set-up. By gradually increasing the temperature and by drawing a vacuum, the solvent was removed.

**Table 1** shows the quantities of monomer and initiator (in grams), the viscosity (measured with an Emilia rheometer; dPa.s, 165°C) and the glass transition temperature (Tg, Mettler TA-3000, 5°C/min system).

<table>
<thead>
<tr>
<th></th>
<th>exp. 1</th>
</tr>
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<tbody>
<tr>
<td>HEA</td>
<td>683.1</td>
</tr>
<tr>
<td>MMA</td>
<td>2396.9</td>
</tr>
<tr>
<td>BMA</td>
<td>220.0</td>
</tr>
<tr>
<td>TRIG 21S</td>
<td>267.9</td>
</tr>
<tr>
<td>TRIG 21S</td>
<td>11.0</td>
</tr>
<tr>
<td>Visc.</td>
<td>450</td>
</tr>
<tr>
<td>Tg</td>
<td>57</td>
</tr>
</tbody>
</table>

where:
1) HEA = hydroxyethyl acrylate
2) MMA = methyl methacrylate
3) BMA = n-butyl methacrylate
4) TRIG 21S = Trigonox 21S (AKZO)
5) quantity of Trigonox 21S as afterinitiator

**Example I**

**Preparation of the crosslinker**

A 2-litre reactor vessel, equipped with a thermometer, a stirrer and a reflux cooler, was filled with 363 grams of haxamethylene di-isocyanate trimer (Tolonate HDT™; Rhône Poulenc) and 39.7 grams of 1,6-hexamethylene di-isocyanate (Tolonate HD™; Rhône Poulenc) (1.89 and 0.47 isocyanate equivalents, respectively). With stirring and while a nitrogen flow was passed through the reactor, the temperature was raised gradually. The reaction mixture was heated to 120°C, after which a total of 163 grams of 1,2,4-triazole (from Chemie Linz) was added in portions. While the portions were added the temperature was held between 120°C and 125°C. Each successive fresh portion of 1,2,4-triazole was not added until the temperature of the reaction mixture had decreased to 120°C again. Ten minutes after the last portion of 1,2,4-triazole had been added the NCO content of the reaction mixture was determined by means of titration. When the NCO content had declined to almost 0, the crosslinker product was removed from the reactor and cooled.
Examples II-VII

[0038] Example I was repeated, with the equivalent ratio between Tolonate HDT and Tolonate HD, being varied as shown in Table 2. The glass transition and melting temperatures for Examples I-VIII are also given in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
</tr>
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<tbody>
<tr>
<td>HDT</td>
<td>8</td>
<td>6.66</td>
<td>6.5</td>
<td>6.2</td>
<td>6</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>HD</td>
<td>2</td>
<td>3.33</td>
<td>3.5</td>
<td>3.8</td>
<td>4</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>105</td>
<td>101</td>
<td>105</td>
<td>105</td>
<td>107</td>
<td>104</td>
<td>101</td>
</tr>
<tr>
<td>Tm (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) HDT = Tolonate HDT™; Rhône Poulenc
2) HD = Tolonate HD™; Rhône Poulenc
3) Tg = glass transition temperature determined by means of DSC, Mettler TA-3000, 5°C/min system
4) Tm = melting point determined by means of DSC, Mettler TA-3000, 5°C/min system

Example VIII

Preparation of binder composition and powder paint

[0039] A powder paint formulation was prepared by mixing 546 grams of polyester resin Uralac P6204 (DSM Resins BV), 54 grams of crosslinker according to Example III, 300 grams of titanium dioxide pigment (KRONOS 2160™), 9 grams of flowing agent (acrylate copolymer on silica; Resiflow PV 5™; Worlee) and 3.5 grams of benzoin (degassing agent). This mixture was extruded by means of a laboratory extruder (Buss Ko-Kneter, PLK 46B) at 130°C with a speed of 60 rpm. The extrudate was cooled, ground and screened. The screen fraction smaller than 90 microns was used as powder paint. This powder paint was sprayed electrostatically onto aluminium panels. The spray-coated panels were enamelled in an oven at 150°C for 30 minutes. The obtained powder coatings showed very advantageous properties such as for example very good flow, high gloss and full impact.

Example IX

[0040] A powder paint formulation was prepared using 432 grams of polyacrylate according to Experiment I, 168 grams of crosslinker according to Example III, 4 grams of flowing agent (acrylate copolymer, BYK 361™; BYK), 2 grams of benzoin (degassing agent) and 0.1 gram of catalyst (butyltintri-2-ethylhexoate; Fastcat 4102™, M&T Chemicals). This mixture was mixed in an extruder at 120°C with a speed of 220 rpm. The extrudate and the powder paint were processed further as described in Example VIII, after which curing took place in 30 minutes at 150°C. The cured coating had a good flow, a good appearance and a flexibility of more than 7 mm according to the 'Erichsen Slow Penetration' test (according to ISO-1520/DIN 53156). The petrol resistance, determined by contacting the coating for 2 hours with a petrol-drenched wad of cotton wool under a piece of glass plate, followed by visual assessment of the coating, was rated as 'very good' because the coating was not damaged.

[0041] The examples show that the combination of very flexible isocyanate compounds Tolonate HDT and Tolonate HD with 1,2,4-triazole as a blocking agent result in crosslinkers that are suitable for use in powder coatings. An essential feature of these kind of crosslinking compounds is that the combination of flexibility and low deblocking temperature can offer powder coating formulations that have good mechanical properties when cured at relatively low temperatures.

Claims

1. A powder paint binder composition comprising a hydroxyl functional polymer and a crosslinker containing blocked isocyanate groups, characterized in that the crosslinker includes (i) a crystalline compound being a blocked 1,6-hexamethylene diisocyanate and ii) an amorphous compound being a blocked 1,6-hexamethylene diisocyanate trimer.

2. A binder composition according to Claim 1, characterized in that the compounds (i) and (ii) are blocked with 1,2,4-triazole.
3. A binder composition according to any one of Claims 1-2, characterized in that the equivalent ratio with respect to equivalents of blocked isocyanate groups between the crystalline compound (i) and the amorphous compound (ii) is between 8:2 and 3:7.

4. A binder composition according to any one of Claims 1-3, characterized in that said polymer is a polyester and/or a polyacrylate.

5. Binder composition according to Claim 4, characterized in that the hydroxyl functional acrylate resin is based on
   i) 8-30 wt.% hydroxyethyl acrylate,
   ii) 5-25 wt.% n-butyl methacrylate and
   iii) 50-80 wt.% methyl methacrylate (i+ii+iii = 100 wt.%).

6. A powder paint comprising a binder composition according to any one of Claims 1-5 and optionally at least one of the following additives selected from the group consisting of pigment, catalyst, flow agent, fillers, stabilizers and degassing agent.

7. Process for the preparation of a powder coating by applying the powder paint according to Claim 6 to a substrate and curing this composition at temperatures between 130°C-170°C in 10-40 minutes.

8. A coated substrate comprising a substrate having wholly or partly coated thereon a powder coating obtained according to Claim 7.

9. Use of a powder paint according to Claim 8 in the preparation of coatings in automotive industry.

Patentansprüche

1. Pulveranstrichstoff-Bindemittel-Zusammensetzung, umfassend ein Hydroxyl-funktionales Polymer und ein Vernetzungsmittel, enthaltend blockierte Isocyanatgruppen, dadurch gekennzeichnet, daß das Vernetzungsmittel (i) eine kristalline Verbindung, die ein blockiertes 1,6-Hexamethylenisocyanat ist, und ii) eine amorphe Verbindung, die ein blockiertes 1,6-Hexamethylenisocyanat-Trimer ist, einschließt.

2. Bindemittel-Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß die Verbindungen (i) und (ii) mit 1,2,4-Triazol blockiert sind.

3. Bindemittel-Zusammensetzung nach einem der Ansprüche 1 bis 2, dadurch gekennzeichnet, daß das Äquivalentverhältnis in Bezug auf die Äquivalente blockierter Isocyanatgruppen zwischen der kristallinen Verbindung (i) und der amorphe Verbindung (ii) zwischen 8:2 und 3:7 liegt.

4. Bindemittel-Zusammensetzung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das Polymer ein Polyester und/oder ein Polyacrylat ist.

5. Bindemittel-Zusammensetzung nach Anspruch 4, dadurch gekennzeichnet, daß das Hydroxyl-funktionale Acrylatharz auf
   i) 8 bis 30 Gew.-% Hydroxyethylacrylat,
   ii) 5 bis 25 Gew.-% n-Butylmethacrylat und
   iii) 50 bis 80 Gew.-% Methylmethacrylat (i+ii+iii = 100 Gew.-%)

basiert.


7. Verfahren zur Herstellung einer Pulverbeschichtung durch Auftragen des Pulveranstrichmittels nach Anspruch 6 auf ein Substrat und Härten dieser Zusammensetzung bei Temperaturen zwischen 130°C bis 170°C in 10 bis 40
8. Beschichtetes Substrat, das eine nach Anspruch 7 erhaltene Pulverbeschichtung ganz oder teilweise darauf be- 
schichtet aufweist.

9. Verwendung eines Pulveranstrichmittels nach Anspruch 8 bei der Herstellung von Beschichtungen in der Kraft- 
fahrzeugindustrie.

Revendications

1. Composition de liant pour peinture en poudre comprenant un polymère à fonction hydroxyle et un agent réticulant 
contenant des groupes isocyanate bloqués, caractérisée en ce que l'agent réticulant comprend (i) un composé 
cristallin qui est un disocyanate de 1,6-hexaméthylène bloqué et (ii) un composé amorphe qui est un trimère de 
disocyanate de 1,6-hexaméthylène bloqué.

2. Composition de liant selon la revendication 1, caractérisée en ce que les composés (i) et (ii) sont bloqués avec 
du 1,2,4-triazole.

3. Composition de liant selon l'une quelconque des revendications 1-2, caractérisée en ce que le rapport d'équivalents 
en ce qui concerne les équivalents de groupes isocyanate bloqués, entre le composé cristallin (i) et le composé 
amorphe (ii) est compris entre 8/2 et 3/7.

4. Composition de liant selon l'une quelconque des revendications 1-3, caractérisée en ce que ledit polymère est un 
polyester et/ou un polyacrylate.

5. Composition de liant selon la revendication 4, caractérisée en ce que la résine acrylate à fonctions hydroxyle est 
à base de

   i) 8-30% en poids d'acrylate d'hydroxyéthyle,
   ii) 5-25% en poids de méthacrylate de n-butyle et
   iii) 50-80% en poids de méthacrylate de méthyle (i+ii+iii = 100% en poids).

6. Peinture en poudre comprenant une composition de liant selon l'une quelconque des revendications 1-5 et éven-
tuellement au moins un des additifs suivants choisis dans l'ensemble consistant en pigment, catalyseur, agent de 
plasticité, charges, stabilisants et agent dégazant.

7. Procédé pour la préparation d'un revêtement en poudre par application de la peinture en poudre selon la reven-
dication 6 à un substrat et durcissement de cette composition à des températures comprises entre 130 et 170 °
en 10 à 40 minutes.

8. Substrat revêtu comprenant un substrat sur lequel est complètement ou partiellement déposé un revêtement en 
poudre obtenu selon la revendication 7.

9. Utilisation d'une peinture en poudre selon la revendication 8 pour la préparation de revêtements dans l'industrie 
automobile.