Process for manufacturing thermosetting resin particles
Verfahren zur Herstellung von wärmehärtenden Harzteilchen
Procédé pour la fabrication de particules de résine thermoréactibles

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GB-A- 2 269 179
US-A- 4 022 622

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BACKGROUND OF THE INVENTION

[0001] This invention relates to a process for manufacturing thermosetting resin particles, particularly for powder coating use, having a narrow particle size distribution.

[0002] There are a number of reports and patent literatures addressing the manufacture of micron size resin particles having a narrow particle size distribution. One of known methods for manufacturing such resin particles is the suspension polymerization method in which vinyl monomers containing an oil-soluble initiator are dispersed as oil droplets in an aqueous medium containing a stabilizer and then polymerized. However, this method gives resin particles having a wide particle distribution under normal stirring conditions. This is because polymer particles tend to adhere to reaction vessel walls or mixing propellers and the particle size distribution depends mainly upon the probability of incidence of agglomerating and splitting of monomer droplets. In order to avoid these phenomena from happening, several methods have been proposed including the use of viscous monomer droplets in the suspension polymerization by dissolving a portion of polymer in the monomer or partly polymerizing the monomer in bulk prior to the suspension polymerization. Other methods include the use of strongly surface active stabilizer or water-insoluble inorganic particles in the dispersing medium. These methods are generally effective to decrease the proportion of coarse particles because of improved mixing efficiency and decreased agglomeration but they are not effective to decrease the proportion of fine particles. Consequently, the particle size distribution represented by the ratio of weight average particle size to number average particle size can be improved only slightly by these methods.

[0003] The seed polymerization and swelling method disclosed in JP-A-58106554 can give linear or crosslinked vinyl polymer particles having a very narrow particle size distribution in which the weight average particle size nearly equals the number average particle size. Unfortunately, this method requires a number of steps for growing polymer particles stepwise making it unsuitable for a large scale industrial application. In addition, it cannot be applied to the manufacture of polymer particles including foreign matters such as pigments.

[0004] JP-A-03200976 discloses a method for manufacturing colored or pigmented polymer particles in which monomers are polymerized in a dispersion in nonaqueous systems or solvent-water mixture systems. Because a large quantity of solvent is used, this method suffers from safety and environmental problems in handling, recovering or otherwise processing used solvents.

[0005] All of the methods discussed supra utilize a radical polymerization of vinyl monomers and produce only vinyl based polymer particles having limited area of use. Furthermore, they are not applicable to the manufacture of particles including those substances having adverse effects on the polymerization reaction, for example, some dyes and pigments or UV absorber and antioxidants abundantly used in automobile finish.

[0006] Recently much interest has been focussed on powder coating in finishing automobile bodies and parts, household electrical apparatuses, building materials and the like for the purposes of eliminating the emission of organic solvents to the environment. Powder coating compositions are generally produced by blending a binder resin with a crosslinker and optionally other additives such as pigments, kneading the mixture under heat to make a molten mass, pulverizing the mass and then classifying pulverized particles. The resulting particles are applied on a substrate using electrostatic spray coating, fluidized bed coating or other methods to form a film, and then baking the film. However, most of prior powder coating compositions have certain defects. Since they tend to cause premature curing before use, chemicals or substances which react at a relatively low temperature cannot be added. Because the weight average particle size of conventional powder coating compositions normally lie at around 30 μm, they are not satisfactory in terms of smoothness, luster and other aesthetic properties of finished films. Attempts have been made to produce finer particles having a weight average particle size of 10 μm or less by means of jet mills or other air stream mills. This approach is found effective to obtain much smoother and thinner films than the films of conventional powder coating compositions. On the other hand, this powder coating composition comprises not only a large portion of microfine particles but also particles of irregular configuration. This makes the powder less free-flowing and increases the incidence of clogging of pneumatic conveyer pipes. Furthermore, it is conventional practice to recover and reuse excessively applied powder successively in the powder coating technology. If the proportion of microfine particles increases in the recovered powder, not only pneumatic transportation will become more difficult but also deposition efficiency of the powder onto the substrate will be greatly impaired.

[0007] Therefore, a need exists for a process for manufacturing powder coating compositions free from above-discussed problems.

SUMMARY OF THE INVENTION

[0008] The present invention provides a process for manufacturing thermosetting resin particles comprising the steps of:
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(a) providing a first water-soluble polymer having a cloud point within the range between 30 °C and 90 °C and a second water-soluble polymer not having any cloud point;
(b) preparing an aqueous suspension of an organic solvent-containing, liquid thermosetting resin composition having a temperature of lower than the cloud point of said first water-soluble polymer, in which said resin composition is suspended as primary particles of oil droplets having a number average particle size of less than 10 microns an aqueous suspension medium containing said first and second water-soluble polymers;
(c) heating said suspension to a temperature higher than said cloud point to allow said primary particles to agglomerate and fuse into secondary particles having a number average particle size from 2 to 20 times greater than that of the primary particles;
(d) distilling off the organic solvent from said secondary particles during or after step (c); and optionally
(e) recovering said secondary particles from the suspension.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0009] This invention utilizes as its principle a surface chemical phenomenon in which a stable suspension of oil droplets in an aqueous solution of a water-soluble polymer having a cloud point becomes less stable when the suspension is heated to a temperature above the cloud point and the oil droplet particles therein grow up to larger secondary particles by agglomeration and fusion. In order to control the particle size or to prevent phase separation, the suspension medium used in this invention also contains a water-soluble polymer not having such cloud point as a temperature-independent stabilizer.

[0010] Typical examples of water-soluble polymers having a cloud point within the range between 30°C and 90 °C include polyvinyl alcohol based polymers having a hydrophobic group or block such as partly saponified polyvinyl alcohol (partly saponified polyvinyl acetate) having a degree of saponification of not greater than 85 %, partly formalized polyvinyl alcohol or ethylene-vinyl acetate copolymer (saponified EVA); cellulose derivatives such as methyleellulose or hydroxypropylcellulose; and non-ionic surfactants such as polyethylene glycol monooalkyl ethers or ethylene oxide-propylene oxide block copolymers. Water-soluble polymers not exhibiting cloud point themselves may be modified to have a cloud point within the above range by adding an electrolyte to their aqueous solutions. Two or more water-soluble polymers having a cloud point may be used in combination.

[0011] Typical examples of water-soluble polymers not having such cloud point include fully saponified polyvinyl alcohol, partly saponified polyvinyl alcohol having a degree of saponification of greater than 85 %, ethylcellulose, hydroxyethyl cellulose, polyethylene glycol and the like.

[0012] The weight ratio of the water-soluble polymer not having cloud point to the water-soluble polymer having cloud point may vary within a wide range depending upon the nature thereof and is generally from 99:1 to 10:90 to control the size of secondary particles in a suitable range.

[0013] The resin component from which particles are made according to this invention may be any resin which is thermocurable and also soluble or swellable in conventional organic solvents. Such resins are well-known in the art and their selection is to be made depending upon the intended use of resin particles and properties required therefor. Examples thereof includes polyesters, (meth)acrylate ester copolymers, aromatic vinyl compound copolymers, epoxy resins, phenol resins, melamine-formaldehyde resins, urea-formaldehyde resins and other thermosetting resins. Resins which are not thermosetting themselves, such as polyester resins, (meth)acrylate ester copolymers or aromatic vinyl compound copolymers are combined with an external crosslinker. Polymers not soluble in a conventional solvent such as polyethylene or polypropylene may be incorporated into the resin particles by dispersing in a solvent-soluble resin component.

[0014] Any organic solvent which is substantially immiscible with water, namely having a solubility in water of less than 10 %, and has a boiling point of lower than 100 °C or is capable of forming an azeotropic mixture with water may be used in this invention. This is because the resin solution should be capable of forming oil droplets in water.

[0015] For use powder coating application, the resin component preferably consists of an epoxy, acrylic or polyester resin in combination with an appropriate crosslinker thereof. Examples of crosslinkers include, as is well-known in the art, polyisocyanic anhydrides, dicyandiamide or acrylic resins for epoxy resins; polyacrylic acids, epoxy resins or melamine resins for acrylic resins; and polyacrylic acids and anhydrides, epoxy compounds, melamine resins or blocked polyisocyanates for polyester resins.

[0016] Particles for powder coating use may optionally contain various pigments such as titanium dioxide, ferric oxide, yellow iron oxide, carbon black, phthalocyanine blue or quinacridon red; surface conditioners such as polysiloxane or acrylic resins; plasticizers; UV absorbers; antioxidants; pigment dispersants; catalysts such as amines, imidazoles or cation polymerization initiators; and other resins. These additives may be dissolved or dispersed in the resin solution.

[0017] According to this invention, the liquid thermosetting resin composition containing an organic solvent is dispersed in an aqueous solution containing a water-soluble polymer having cloud point and a water-soluble polymer not having cloud point in step (b) at a temperature below said cloud point so that the mixture forms a suspension in which
the liquid resin composition is suspended as primary particles of oil droplets having a number average particles size of less than 10 μm. The proportions of the water-soluble polymer having cloud point and the water-soluble polymer not having cloud point may be varied, as stated before, depending upon the nature of particular liquid resin composition and the desired particle size. In order to facilitate mixing, the total concentration of the water-soluble polymers in the aqueous solution is preferably from 0.2% to 20% by weight, and the ratio of the liquid resin composition to the aqueous solution is preferably from 1:0.5 to 1:3. Mixing of these two components may be accomplished by means of a homogenizer when their viscosities are relatively low. When their viscosities are relatively high, mixing may be accomplished by means of a universal mixer or a planetary mixer. In cases where the liquid resin composition and the aqueous solution do not initially form a suspension, the liquid resin composition is dispersed first in an aqueous solution solely containing the water-soluble polymer not having cloud point optionally in combination with a conventional surfactant to make a suspension. Thereafter the water-soluble polymer having cloud point may be added to the suspension. The suspension is adjusted to a final resin composition concentration of from 10% to 50% by weight by diluting, where necessary, with deionized water.

[0019] The temperature at which the solvent is distilled off in step (d) may be easily controlled by applying vacuum or reduced pressure. Therefore, resin particles containing a component susceptible to a chemical reaction itself or with another component at a predetermed temperature, as in case of powder coating compositions, can be produced by using a water-soluble polymer having a cloud point substantially lower than the reaction temperature and distilling off the organic solvent at a temperature below the reaction temperature in vacuo.

[0020] The present invention thus enables to control oil droplets in the suspension to be of relatively uniform size.

Although the present invention is not bound to a particular theory or principle, the mechanism behind the formation of relatively uniform size of particles is postulated as follows. The water-soluble polymer having a cloud point present as a stabilizer of oil droplets in the dispersion, becomes less soluble in water and less effective to stabilize the suspension as the temperature increases above the cloud point. As a consequence the total surface area of dispersed phase decreases and finer particles tend to agglomerate with each other into larger secondary particles to accomodate the decrease in the total surface area of dispersed phase. Since finer particles have larger specific surface areas than coarse particles, they will preferentially agglomerate into larger secondary particles. This contributes to a narrow particle size distribution of secondary particles even when starting from primary particles having wider particle size distributions.

[0021] After the organic solvent contained in the second particles is removed, the final particles may be recovered from the suspension by any conventional means such as filtering or centrifugation, and then dried. The final particles thus obtained generally have a ratio of weight average particle size to number average particle size of less than 2.

[0022] In addition to a narrow particle size distribution, the present invention can achieve other significant advantages. For example, the present invention enables the melting point and/or pigment dispersibility of the final particles to be easily adjustable. It also enables to modify the surfaces of particles to have various functional groups. Contrary to the prior art methods, it is possible to incorporate into the particles an additive which would adversely affect the polymerization reaction of monomers or use a variety of resins, crosslinkers and additives such as epoxy resins, acrylic resins, polyester resins, polycarboxylic acids, blocked polyisocyanate, pigments, surface conditioners or UV absorbers.

[0023] For powder coating application, since the resin particles produced by the present invention not only have a predetermined particle size but also consist mainly of spherical particles with lesser proportions of microfine and irregular shape particles than particles produced by the prior art methods, they are free-flowing and produce a thin coating film having excellent appearance properties.

[0024] The present invention can also be applied to the manufacture of particles of thermoplastic resins. For example, the present invention could be applied to the production of toners for electrophotography by mixing a thermoplastic resin such as styrene/acrylic or polyester resins with a pigment such as carbon black and a electrostatic charge controlling agent such as azo- or nigrosine dyes.

[0025] The following examples are given for illustrative purpose only but not for limiting purposes. All parts and percents therein are by weight unless otherwise specified. Production Example 1
Resin solution A

[0026] A reactor equipped with a stirrer, condenser, thermometer and nitrogen gas tube was charged with 63 parts of xylene and heated to 130°C. To this was added the following monomer mixture over 3 hours under nitrogen gas atmosphere.

<table>
<thead>
<tr>
<th>Material</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycidyl methacrylate</td>
<td>40</td>
</tr>
<tr>
<td>Styrene</td>
<td>25</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>25</td>
</tr>
<tr>
<td>Isobutyl methacrylate</td>
<td>10</td>
</tr>
<tr>
<td>t-Butyl peroctoate</td>
<td>3</td>
</tr>
</tbody>
</table>

[0027] Thereafter the mixture was maintained at the same temperature for 30 minutes. After adding 1 part of t-butyl peroctoate over 30 minutes, the mixture was maintained at the same temperature for 1 hour and then cooled to room temperature.

Production Example 2

Resin solution B

[0028] A reactor equipped with a stirrer, condenser and thermometer was charged with the following materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isophthalic acid</td>
<td>35</td>
</tr>
<tr>
<td>Phthalic anhydride</td>
<td>31</td>
</tr>
<tr>
<td>Neopentyl glycol</td>
<td>41</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>5</td>
</tr>
<tr>
<td>Dibutyltin oxide</td>
<td>0.06</td>
</tr>
</tbody>
</table>

[0029] The mixture was heated to 190°C and then to 240°C over 3 hours while removing water. The condensation reaction was then continued until an acid number of 5 was reached. After the reaction, the product was cooled to 100°C and dissolved in 100 parts of xylene.

Example 1

[0030] A thermosetting resin composition was produced by mixing the following materials in a sand grind mill.

<table>
<thead>
<tr>
<th>Material</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin solution A</td>
<td>84.70</td>
</tr>
<tr>
<td>Curing agent (1,10-decanedicarboxylic acid sold by Ube Industries, Ltd.)</td>
<td>12.70</td>
</tr>
<tr>
<td>Polysiloxane surface conditioner (YF-3919 sold by Toshiba Silicone Co., Ltd)</td>
<td>0.10</td>
</tr>
<tr>
<td>Benzoin</td>
<td>0.30</td>
</tr>
<tr>
<td>Material</td>
<td>Parts</td>
</tr>
<tr>
<td>------------------------------</td>
<td>-------</td>
</tr>
<tr>
<td>UV absorber</td>
<td>1.20</td>
</tr>
<tr>
<td>Hindered amine antioxidant</td>
<td>1.00</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>

[0031] Separately, an aqueous solution was prepared by dissolving 6 parts of GOHSENOL GH-20 (polyvinyl alcohol having a degree of saponification of 88 % sold by The Nippon Synthetic Chemical Industry Co., Ltd.) and 4 parts of GOHSENOL KL-05 (polyvinyl alcohol having a degree of saponification of 80 % sold by The Nippon Synthetic Chemical Industry Co., Ltd.) in 90 parts of deionized water.

[0032] The above resin composition and the aqueous solution were mixed in a homogenizer at $10^4$ r.p.m. to make a suspension. The particle sizes of suspended droplets were determined using a Coulter counter. The weight average particle size was 4.6 μm and the number average particle size was 2.1 μm.

[0033] The suspension was then diluted with 300 parts of deionized water and placed in a container equipped with a stirrer, temperature control means, reflux condenser and pressure reducing means. Then the suspension was heated to 70 °C under a reduced pressure of 160 Torr (0.21 bar) until the solvent in the dispersed phase was completely removed and cooled to room temperature. The resin particles thus produced were recovered by centrifugation, dried and tested for their particle size using a Coulter counter. The weight average particle size was 8.6 μm and the number average particle size was 6.2 μm. Thus, the particle size distribution curve was very sharp.

Example 2

[0034] Example 1 was followed except that the aqueous water-soluble polymer solution was replaced with a solution of 10 parts of GOHSENOL GH-20 and 2 parts of METOLOSE 65SH (methyl cellulose sold by Shin-etsu Chemical Co., Ltd.) in 82 parts of deionized water. The weight average particle size and the number average particle size of oil droplets in the resulting suspension were 5.1 μm and 2.3 μm, respectively.

[0035] The suspension was then diluted with 300 parts of deionized water and placed in a container equipped with a stirrer, temperature control means, reflux condenser and pressure reducing means. After removing about 90 % of the solvent contained in the dispersed phase by applying a reduced pressure of 20 Torr (0.026 bar), the remaining solvent was completely removed by heating the suspension to 70 °C at a reduced pressure of 160 Torr (0.21 bar). After cooling, the suspension was centrifuged and the separated particles were dried. The resin particles were found to possess a weight average particle size of 8.0 μm and a number average particle size of 6.8 μm, exhibiting a sharp particle size distribution curve.

Example 3

[0036] Example 1 was followed except that the aqueous water-soluble polymer solution was replaced with a solution of 10 parts of GOHSENOL GH-20 and 0.5 parts of METOLOSE 65SH in 82 parts of deionized water. The weight average particle size and the number average particle size of oil droplets in the suspension were 4.7 μm and 2.2 μm, respectively.

[0037] The suspension was diluted with 300 parts of deionized water and then placed in the same container as used in the preceding Examples. After removing about 90 % of the solvent from the dispersed phase by applying a reduced pressure of 20 Torr (0.026 bar), the remaining solvent was completely removed by heating the suspension to 70 °C at a reduced pressure of 160 Torr (0.21 bar). After cooling, the suspension was centrifuged and the separated particles were dried. The resin particles were found to possess a weight average particle size of 8.6 μm and a number average particle size of 4.4 μm, exhibiting a sharp particle size distribution curve.

Comparative Example 1

[0038] Example 1 was followed except that the aqueous water-soluble polymer solution was replaced with a solution of 10 parts of GOHSENOL GH-20 in 82 parts of deionized water. The weight average particle size and the number average particle size of oil droplets in the suspension were 8.6 μm and 3.3 μm, respectively.

[0039] The suspension was diluted with 300 parts of deionized water and then placed in the same container as used in the preceding Examples. After removing about 90 % of the solvent from the dispersed phase by applying a reduced pressure of 20 Torr (0.026 bar), the remaining solvent was completely removed by heating the suspension to 70 °C at a reduced pressure of 160 Torr (0.21 bar). After cooling, the suspension was centrifuged and the separated particles
were dried. The powder coating composition thus produced were found to possess a weight average particle size of 8.9 μm and a number average particle size of 3.4 μm, exhibiting a broad particle size distribution curve. Most of particles were of sizes of oil droplets initially formed as primary particles.

Example 4

[0040] A thermosetting resin composition was produced by mixing the following materials in a sand grind mill.

<table>
<thead>
<tr>
<th>Material</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin solution B</td>
<td>80</td>
</tr>
<tr>
<td>Epoxy resin (EPOTOHTO YD-014 sold by Toto Kaisei K.K.)</td>
<td>5</td>
</tr>
<tr>
<td>Methyl isobutyl ketone</td>
<td>10</td>
</tr>
<tr>
<td>Curing agent (blocked polyisocyanate)</td>
<td>10</td>
</tr>
<tr>
<td>Benzoin</td>
<td>0.3</td>
</tr>
<tr>
<td>Polysiloxane surface conditioner</td>
<td>0.1</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>20</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

[0041] Separately, a water-soluble polymer solution was produced by dissolving 4 parts of GOHSENOL GH-20 and 3 parts of GOHSENOL KL-05 in 93 parts of deionized water.

[0042] The above resin composition and the aqueous solution were mixed in a planetary mixer to obtain a suspension of oil droplets having a weight average particle size of 4.2 μm and a number average particle size of 2.0 μm.

[0043] The suspension was then diluted with 250 parts of deionized water and 50 parts of a 5% aqueous solution of hydroxypropyl cellulose, and then placed in the same container as used in the preceding Examples. After removing about 90% of the solvent from the dispersed phase by applying a reduced pressure of 20 Torr (0.026 bar), the remaining solvent was completely removed by heating the suspension to 70°C at a reduced pressure of 160 Torr (0.21 bar). After cooling, the suspension was centrifuged and the separated particles were dried. The particles were found to possess a weight average particle size of 9.6 μm and a number average particle size of 7.1 μm, exhibiting a sharp particle size distribution curve.

Example 5

[0044] Example 4 was followed except that the aqueous solution was replaced with a solution containing 2 parts of GOHSENOL GH-20 and 8 parts of GOHSENOL KL-05 in 93 parts of deionized water. A suspension of oil droplets having a weight average particle size of 4.5 μm and a number average particle size of 2.1 μm was obtained.

[0045] The suspension was diluted with 250 parts of deionized water and 50 parts of a 5% aqueous solution of hydroxypropyl cellulose, and placed in a container as used in the preceding Examples. After removing about 90% of the solvent contained in the dispersed phase by applying a reduced pressure of 20 Torr (0.026 bar), the remaining solvent was completely removed by heating the suspension to 70°C at a reduced pressure of 160 Torr (0.21 bar). After cooling, the suspension was centrifuged and the separated particles were dried. The particles thus produced were found to possess a weight average particle size of 15.3 μm and a number average particle size of 7.9 μm, exhibiting a sharp particle size distribution curve.

Comparative Example 2

[0046] Example 4 was followed except that the aqueous solution was replaced with a solution of 10 parts of GOHSENOL GH-20 in 82 parts of deionized water to produce a suspension of oil droplets having a weight average particle size of 10.9 μm and a number average particle size of 3.2 μm.

[0047] The suspension was diluted with 300 parts of deionized water and placed in the container as used in the preceding Examples. After removing about 90% of the solvent contained in the dispersed phase by applying a reduced pressure of 20 Torr (0.026 bar), the remaining solvent was completely removed by heating the suspension to 70°C at a
reduced pressure of 160 Torr (0.21 bar). After cooling, the suspension was centrifuged and the separated particles were dried. The particles thus produced were found to possess a weight average particle size of 11.3 μm and a number average particle size of 3.2 μm, exhibiting a wide particle size distribution curve. Most of particles were of sizes of oil droplets initially formed as primary particles.

Comparative Example 3

[0048] Example 4 was followed except that the aqueous solution was replaced with a solution containing 8 parts of GOHSENOL KL-05 and 2 parts of METOLOSE 65SH in 82 parts of water. A suspension of oil droplets having a weight average particle size of 4.2 μm and a number average particle size of 1.7 μm was obtained.

[0049] After diluting with 300 parts of deionized water, the suspension was placed in the same container as used the preceding Examples. After removing about 90 % of the solvent contained in the dispersed phase by applying a reduced pressure of 20 Torr (0.026 bar), the remaining solvent was completely removed by heating the suspension to 70°C at a reduced pressure of 20 Torr (0.026 bar). The product contained a large amount of cakes or coarse particles, making it unusable for powder coating.

[0050] The powder coating compositions produced in Examples 1-5 and Comparative Examples 1-2 were tested for their performance. Each composition was applied electrostatically on a steel plate and baked at 160°C for 30 minutes to produce a cured film of 50 μm film thickness. The appearance was evaluated in terms of NSIC (%) measured by a reflected image distinctiveness meter (Suga Testing Instrument Co., Ltd.).

[0051] Applicator systems used in the powder coating technology normally comprise a powder feeder (fluidized bed), injector, conveying hose and spray gun. Workability of powders of Examples and Comparative Examples was evaluated by operating the above applicator for 1 hour continuously with each powder, and judged based on the volume of powder accumulated in the injector and the hose according to the following schedule.

| Very good : | Not accumulated at all. |
| Good : | Not substantially accumulated. |
| Bad : | Injector or hose was clogged. |

[0052] The test results are shown in Table 1.

<table>
<thead>
<tr>
<th>Evaluation of powder coating compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Weight average particle size, μm</td>
</tr>
<tr>
<td>Number average particle size, μm</td>
</tr>
<tr>
<td>Appearance, NSIC in %</td>
</tr>
<tr>
<td>Workability</td>
</tr>
</tbody>
</table>

Claims

1. A process for manufacturing thermosetting resin particles comprising the steps of

(a) providing a first water-soluble polymer having a cloud point within the range between 30 °C and 90 °C and a second water-soluble polymer not having any cloud point;
(b) preparing an aqueous suspension of an organic solvent-containing, liquid thermosetting resin composition having a temperature of lower than the cloud point of said first water-soluble polymer, in which said resin composition is suspended as primary particles of oil droplets having a number average particle size of less than 10 microns in an aqueous suspension medium containing said first and second water-soluble polymers;
(c) heating said suspension to a temperature higher than said cloud point to allow said primary particles to agglomerate and fuse into secondary particles having a number average particle size from 2 to 20 times

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greater than that of the primary particles; and
(d) distilling off the solvent from said secondary particles during or after step (c).

2. The process according to claim 1 further comprising the step of recovering said secondary particles from the suspension.

3. The process according to claim 1 wherein the ratio of said polymer having a cloud point to said polymer not having cloud point is from 1:99 to 90:10 by weight.

4. The process according to claim 1 wherein said water-soluble polymer having a cloud point is selected from polyvinyl alcohols having a degree of saponification of less than 85%, partly formalized polyvinyl alcohols, ethylene-vinyl alcohol copolymers, methyl cellulose, hydroxypropyl cellulose, polyethylene glycol monoalkyl ethers, or ethylene oxide-propylene oxide block copolymers.

5. The process according to claim 1 wherein said water-soluble polymer not having cloud point is selected from polyvinyl alcohols having a degree of saponification of greater than 85%, ethyl cellulose, hydroxyethyl cellulose or polyethylene glycols.

6. The process according to claim 1 wherein said organic solvent has a boiling point of lower than 100 °C or is removable by azeotropic distillation with water.

7. The process according to claim 1 wherein the concentration of said first and second water-soluble polymers in said aqueous suspension medium is from 0.02 to 20 % by weight.

8. The process according to claim 1 wherein the final concentration of said liquid thermosetting resin composition in said suspension is from 10 to 50 % by weight.

9. The process according to claim 1 wherein said liquid thermosetting resin composition comprises a binder resin and a crosslinker.

10. The process according to claim 9 wherein said binder resin is an epoxy, acrylic or polyester resin.

11. A powder coating composition comprising the thermosetting resin particles produced by the process of claim 9.

12. A powder coating composition comprising the thermosetting resin particles produced by the process of claim 10.

Patentansprüche

1. Verfahren zur Herstellung wärmehärtbarer Harzeilchen, bei dem man
(a) ein erstes wasserlösliches Polymer mit einem Trübungspunkt im Bereich zwischen 30 °C und 90 °C und ein zweites wasserlösliches Polymer ohne Trübungspunkt bereitstellt;
(b) eine wässrige Suspension einer ein organisches Lösungsmittel enthaltenden, flüssigen wärmehärtbaren Harzzusammensetzung mit einer Temperatur von weniger als dem Trübungspunkt des ersten wasserlöslichen Polymers herstellt, in welcher die Harzzusammensetzung als primäre Öltröpfchen-Teilchen mit einer zahlenmittleren Teilchengröße von weniger als 10 μm in einem wässrigen Suspensionsmedium suspendiert ist, das das erste und das zweite wasserlösliche Polymer enthält;
(c) die Suspension auf eine Temperatur von mehr als dem Trübungspunkt erwärmt, um die primären Teilchen zu agglomerieren und in sekundäre Teilchen mit einer zahlenmittleren Teilchengröße, die das zwei-bis zwanzigfache derjenigen der primären Teilchen beträgt, zu verschmelzen; und
(d) von den sekundären Teilchen während oder nach dem Schritt (c) das Lösungsmittel abdestilliert.

2. Verfahren nach Anspruch 1, bei dem man außerdem die sekundären Teilchen aus der Suspension isoliert.

3. Verfahren nach Anspruch 1, wobei das Gewichtsverhältnis des Polymers mit Trübungspunkt zu dem Polymer ohne Trübungspunkt 1:99 bis 90:10 beträgt.

4. Verfahren nach Anspruch 1, wobei das wasserlösliche Polymer mit Trübungspunkt ausgewählt ist unter Polyvinyl-
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5. Verfahren nach Anspruch 1, wobei das wasserlösliche Polymer ohne Trübungspunkt ausgewählt ist unter Polyvinylalkoholen mit einem Verseifungsgrad von mehr als 85 %, Ethylenkolloide, Hydroxyethylcellulose oder Polyethylenkolloid.

6. Verfahren nach Anspruch 1, wobei das organische Lösungsmittel einen Siedepunkt von weniger als 100 °C aufweist oder durch azeotrope Destillation mit Wasser entfernt ist.

7. Verfahren nach Anspruch 1, wobei die Konzentration des ersten und zweiten wasserlöslichen Polymers im wässrigen Suspensionsmedium 0,02 bis 20 Gew.-% beträgt.

8. Verfahren nach Anspruch 1, wobei die Endkonzentration der flüssigen wärmehärtbaren Harzzusammensetzung in der Suspension 10 bis 50 Gew.-% beträgt.

9. Verfahren nach Anspruch 1, wobei die flüssige wärmehärtbare Harzzusammensetzung ein Binderharz und einen Vernetzer umfasst.


1. Procédé de fabrication de particules de résine thermodurcissables comprenant les étapes consistent à :

(a) apporter un premier polymère hydrophorable ayant un point de rosée compris entre 30 °C et 90 °C et un second polymère hydrophorable n'ayant pas de point de rosée;

(b) préparer une suspension aqueuse d'une composition de résine liquide thermodurcissable contenant un solvant organique, ayant une température inférieure au point de rosée dudit premier polymère hydrophorable, dans laquelle ladite composition de résine est suspendue sous forme de particules primaires de gouttelettes d'huile ayant une taille de particule moyenne inférieure à 10 microns dans un milieu de suspension aqueux contenant les dits premier et second polymères hydrophorables;

(c) chauffer ladite suspension à une température supérieure au dit point de rosée pour permettre auxdites particules primaires de s'agglomérer et de fusionner en particules secondaires ayant une taille de particule moyenne de 2 à 20 fois supérieure à celle des particules primaires; et

(d) distiller le solvant desdites particules secondaires durant ou après l'étape (c).

2. Procédé selon la revendication 1 comprenant en outre l'étape de récupération desdites particules secondaires dans la suspension.

3. Procédé selon la revendication 1 dans lequel le rapport entre ledit polymère ayant un point de rosée et ledit polymère n'ayant pas de point de rosée est compris entre 1,99 et 90:10 en poids.

4. Procédé selon la revendication 1 dans lequel ledit polymère hydrophorable ayant un point de rosée est choisi parmi un alcool polyvinylique ayant un degré de saponification inférieur à 85 %, des acols polyvinyliques partiellement formalisés, des copolymères d'alcool vinyle et d'éthylène, la méthyl cellulose, l'hydroxypropyl cellulose, les éthers monoalkyles de polyalkyléne glycol, ou les copolymères bloc d'oxyde de propylène et d'oxyde d'éthylène.
5. Procédé selon la revendication 1 dans lequel le dit polymère hydrosoluble n'ayant pas de point de rosée est choisi parmi les alcools polyvinyliques ayant un degré de saponification supérieur à 85 %, l'éthyl cellulose, l'hydroxyéthyl cellulose ou les polyéthylène glycols.

6. Procédé selon la revendication 1 dans lequel le dit solvant organique a un point d'ébullition inférieur à 100°C ou peut être éliminé par distillation azéotropique avec de l'eau.

7. Procédé selon la revendication 1 dans lequel la concentration desdits premier et second polymères hydrosolubles dans le dit milieu de suspension aqueux est comprise entre 0,02 et 20 % en poids.

8. Procédé selon la revendication 1 dans lequel la concentration finale en ladite composition de résine thermordurcissable liquide dans ladite suspension est comprise entre 10 et 50 % en poids.

9. Procédé selon la revendication 1 dans lequel ladite composition de résine thermordurcissable liquide comprend une résine liante et un agent de rétication.

10. Procédé selon la revendication 9 dans lequel ladite résine liante est une résine époxy, acrylique ou polyester.

11. Composition de revêtement en poudre comprenant les particules de résine thermordurcissables obtenues par le procédé de la revendication 9.

12. Composition de revêtement en poudre comprenant les particules de résine thermordurcissables obtenues par le procédé de la revendication 10.