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(54) **PROCESS FOR COATING A BOARD- OR PAPER-LIKE SUBSTRATE WITH A POWDER PAINT COMPOSITION**

VERFAHREN ZUR BESCHICHTUNG VON EINEM KARTON- ODER PAPIERÄHNLICHEN
SUBSTRAT MITTELS EINER PULVERLACKZUSAMMENSETZUNG

PROCEDE D'ENDUCTION D'UN SUBSTRAT DE TYPE CARTON OU PAPIER AU MOYEN D'UNE
COMPOSITION DE PEINTURE EN POWDRE

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US-A- 4 076 857 **US-A- 5 039 587**

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- **TAPPI, vol. 38, no. 10, October 1955, NEW YORK, US, pages 607-609, XP000600755 R.B.REIF: "An electrostatic process for applying dry coatings on paper"**
- **J.F.HUGHES: 'Particle charging for powder coating' May 1986, pages 10 - 13**

EP 0 895 552 B1

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Description

[0001] The invention relates to a process for coating a board- or paper-like substrate with a powder paint composition and use of the process in the application of overprint varnishes.

[0002] In industrial applications varnishing of, for example, cellulose based sheets and webs is usually carried out using solvent or water-based varnishes. The solvent-based varnishes have as a disadvantage the evaporation of solvents into the atmosphere. Because of environmental reasons emission of solvents has to be reduced drastically. The water-based varnishes have as a disadvantage that they need much energy for drying. To achieve the highest possible gloss the use of calanders is suitable. This separate step is costly and limits the process speed.

[0003] Alternatively, liquid UV-curable varnishes are used to overcome these difficulties. However, this group of materials is often rejected because of their sensibilizing and irritating character due to the applied monomers, which are the main components of these coating liquids. Another disadvantage of this coating technology can be that the smell makes the coating unsuitable for food packaging.

[0004] GB-A-2056885 discloses a process for coating a cellulose fibre substrate like cardboard with a powder paint composition and curing by radiant heat. Generally a binder system for a powder paint composition consists of a resin and a crosslinker. A disadvantage of the process according to GB-A-2056885 is the limited capacity of the applied powder paint spray guns which imposes a restriction on the rate of application of powder paint to the substrate. Another disadvantage is that it is very difficult to achieve coatings having a layer thickness below 15µm.

[0005] A further disadvantage is the major thermal load imposed on the heat-sensitive substrate during curing of the powder paint composition.

[0006] It is the object of the present invention to provide a process for coating a board or paper-like substrate (which substrate can already be precoated) at process speeds of substrates between, for example, 1 and 400 meter substrate/minute, giving a high quality coating with a thickness between for example 1 µm and 100 µm.

[0007] The invention is characterized in that powder paint particles are first charged by friction or induction in the presence of magnetic or non-magnetic particles, are next transported and then applied to the substrate, or applied to a transfer medium and are then transferred to the substrate, by means of an electric field between the substrate respectively the transfer medium and the means of transport, whereafter the powder paint composition is cured or fused into a powder coating wherein the powder paint particles are based on solid particles of a radiation curable binder system.

[0008] Suitable radiation curable binder systems include for example a polymer having unsaturated groups and a cationic curable system based on, for example epoxy resins.

[0009] Preferably, the radiation curable binder system comprises a polymer having unsaturated groups.

[0010] Preferably, said polymer having unsaturated groups has a degree of unsaturation between about 200 and about 1800 grams of polymer per mole of unsaturated group.

[0011] Charging of the powder paint particles by friction or induction, transport or conveying and application to the substrates can be effected using processes commonly known in photocopying technology or laser printer technology (which processes are elucidated in, for example, L.B. Schein, Electrography and Development Physics, pages 32-244, Volume 14, Springer Series in Electrophysics 1988; the disclosure of which is incorporated herein by reference).

[0012] According to a preferred embodiment of the invention the powder paint particles are mixed with magnetic or non-magnetic carrier particles to obtain friction charging whereupon the mixture is transported and the powder paint particles are applied to the substrate or a transfer medium, and subsequently transferred to the substrate, by means of an electric field between the substrate or the transfer medium and the means of transport.

[0013] Depending on the conductivity of the substrate the electric field between the substrate and the transfer medium or means of transport can be applied with suitable methods like for instance a corona discharge or a moving or fixed counterelectrode (see for instance Schein, pp. 36-37 and 47).

[0014] In case a transfer medium is used, the powder paint particles are first applied to the transfer medium by means of an electric field, transported to the substrate by the transfer medium and then applied to the substrate by, for example, electrical, electrostatic or mechanical forces. Thermal processes can also be used in this application step.

[0015] The present process allows powder paint particles to be applied to coated or uncoated board- or paper-like substrates such as, for example, cardboard, hardboard, fibre board for example MDF, particle board, chipboard, plywood, veneer, block board (which board products can be paperfaced), wood, timber and paper at rates up to, for instance, 400 meters of substrate/minute with a film thickness of the cured film of between, for example, 1 µm and 100 µm.

[0016] Preferably, the polymer having unsaturated groups has a molecular weight (Mn) between about 800 and about 6800 grams/mole and a viscosity between 1 dPas and 800 dPas (measured with an Emila rheometer at 165°C).

[0017] Preferred polymers are unsaturated polyesters, unsaturated polyacrylates and acrylated polyesters.

[0018] Preferably, the unsaturated polymer has a degree of unsaturation between 300 and 1800 grams per mole of unsaturated group (WPU), a molecular weight (Mn) between about 800 and about 6800 and a viscosity between 1

dPas and 400 dPas. The preferred degree of unsaturation for an unsaturated polyester is between 500 and 1500 grams per mole of unsaturated group.

[0019] The molecular weight (Mn) is preferably between about 2500 and about 4500 grams/mole.

[0020] The unsaturated polyester can be (semi)crystalline or amorphous.

5 [0021] In general, the glass transition temperature (Tg) of the amorphous resin is higher than 40°C. Semi-crystalline resins have a Tg and a melting point (Tm), and Tg is lower than Tm.

[0022] The melting point of the (semi)crystalline unsaturated polyester is between about 40°C and about 180°C, and preferably, is between about 60°C and about 140°C. The melting point and the melting range are discussed at pages 36, 286 and 295 of Misev, Powder Coatings, Chemistry and Technology Wiley 1991.

10 [0023] Thermosetting powder coatings that are based on unsaturated polyester are described in Misev, Powder Coatings, Chemistry and Technology, at pages 167-170.

[0024] Preparation of the unsaturated polyester can be carried out in a single-step process in which unsaturated polyfunctional carboxylic acids and glycols are heated to a temperature, for example, between about 180°C to about 230°C for between about 6 hours to about 15 hours.

15 [0025] Preparation of the unsaturated polyester can also be carried out in a two-step process in which saturated glycols and saturated polyfunctional carboxylic acids are esterified in a first step at, for example, between about 230°C to about 250°C for between about 2 hours to about 8 hours. In a second step, saturated or unsaturated glycols and acids, or mixtures thereof, are esterified at, for example between about 180°C and 220°C for between about 2 to about 8 hours.

20 [0026] In general, the unsaturated polyester is obtainable from the condensation of one or more aliphatic or cycloaliphatic mono-, di- or polyfunctional alcohols, or mixtures thereof, one or more aliphatic, cycloaliphatic, or aromatic di- or polyfunctional carboxylic acids, or mixtures thereof, and if desired, a monofunctional carboxylic acid or the corresponding ester of this monofunctional carboxylic acid.

25 [0027] Examples of suitable alcohols and glycols include, among others, benzyl alcohol, ethylene glycol, propylene glycol, neopentylglycol, butanediol, hexanediol, dimethylol cyclohexane, diethylene glycol, glycerol, trimethylol propane, pentaerythritol, dipentaerythritol, or mixtures thereof. Instead of an alcohol or glycol, or together with an alcohol or glycol, one or more epoxy compounds such as, for example, ethylene oxide, propylene oxide, allyl glycidyl ether, or mixtures thereof, can be used.

30 [0028] Examples of suitable di- or polyfunctional carboxylic acids include maleic acid, fumaric acid, itaconic acid, citraconic acid, malonic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, 1,4-cyclohexane dicarboxylic acid, hexahydrophthalic acid, hexachloroendomethylenetetrahydrophthalic acid, dichlorophthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, or mixtures thereof.

[0029] Fumaric acid, maleic acid, or a mixture thereof, is preferred.

35 [0030] The carboxylic acids can also be applied in the corresponding anhydride form, so that, for example, tetrahydrophthalic anhydride, maleic anhydride, phthalic anhydride, or mixtures thereof can be used.

[0031] If desired, the unsaturated polyester can also be obtained from saturated or unsaturated monofunctional carboxylic acids, or mixtures thereof. These monofunctional carboxylic acids include, for example, synthetic or natural fatty acids having 2 to 36 carbon atoms. Corresponding esters of monofunctional alcohols such as glycerol are used for esterification. Examples of suitable monofunctional carboxylic acids include, among others, lauric, stearic, oleic, 40 linoleic, benzoic, acrylic, methacrylic acid, or mixtures thereof. The unsaturated polyester can also contain dicyclopentadiene.

[0032] If the unsaturated polyester is hydroxyl-functionalized, then the hydroxyl number of the polyester is usually between about 18 mg KOH/gram of resin and about 75 mg KOH/gram of resin.

45 [0033] If the unsaturated polyester is acid-functionalized, the acid number is usually between about 18 mg KOH/gram of resin and about 75 mg KOH/gram of resin.

[0034] Suitable acrylate polymers include, for instance, acrylate polymers having several side chains containing unsaturated groups.

50 [0035] These polymers can be obtained by means of a two-step process. In the first step an acrylate polymer is prepared by a conventional polymerization process, in which also a certain proportion of functional monomer is copolymerized to obtain a functionalized acrylate polymer. This functional monomer, which usually is present in amounts of between 3 and 60 wt. %, can be, for example, an epoxy functionalized monomer such as glycidyl (meth)acrylate; an acid functionalized monomer such as, for instance, (meth)acrylic acid, a hydroxy functionalized monomer such as, for instance hydroxyethyl(meth)acrylate; or an isocyanate functionalized monomer such as, for instance, TMI (meta-isopropenyl- α - α -dimethylbenzyl-isocyanate).

55 [0036] In the second step for the acrylate synthesis, an addition reaction, is carried out between the functional groups of the acrylate polymer which is prepared in the first step and a compound having both a functional group capable of reacting with the functional groups and also an unsaturated group in the side chain.

[0037] For the addition reaction of this second step, the functionalized acrylate resin can be dissolved in a solvent

such as for example toluene, xylene and/or butyl acetate. The compound having the unsaturated group, is added at temperatures between, for example, 50°C and 150°C and next, stirring takes place for some hours. Progress of the reaction can be monitored by means of titrations of, for instance, acid groups or isocyanate groups. Addition reactions of this second step are, for instance, between a compound having an acid group and an epoxy functional acrylate polymer, a compound having a hydroxyl group and an isocyanate functionalized acrylate polymer, a compound having an isocyanate group and a hydroxyl functionalized acrylate polymer, a compound having an anhydride group and a hydroxyl functionalized acrylate polymer or a compound having an epoxy group and an acid functionalized acrylate polymer.

[0038] It is preferred to allow an epoxy functionalized acrylate polymer to react with (meth)acrylic acid.

[0039] The unsaturated side chain can have, for example, methacrylate ester, allyl, vinyl, vinyl ether, or anhydride groups, or mixtures thereof. Suitable compounds that are allowed to react with the functionalized acrylate copolymer are, for example, methacrylic acid, glycidyl methacrylate, TMI, allylglycidyl ether, hydroxybutylvinyl ether, maleic anhydride, or mixtures thereof.

[0040] The unsaturated acrylate polymer can also be obtained by means of a multi-step process. For example, one of the isocyanate groups of a diisocyanate compound such as, for example, isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI) or methylenebiscyclohexylisocyanate (hydrogenated MDI) is allowed to react with a methacrylate monomer having the hydroxyl functionality. The resulting urethane compound, which contains isocyanate and methacrylate groups for further reaction, can subsequently be allowed to react with, for example, an acrylate copolymer having the hydroxyl functionality. This acrylate copolymer can be prepared using, for example, hydroxyethyl methacrylate as a functionalized monomer.

[0041] Depending on the binder system a crosslinker has to be applied or can optionally be applied.

[0042] A preferred crosslinking agent for the radiation curable binder composition according to the present invention is an oligomer or polymer having one or more vinyl ether, allyl, vinyl ester, or (meth)acrylate groups. More preferably an oligomer or polymer having at least two vinyl ether groups is applied.

[0043] The crosslinking agent having vinyl ether groups is preferably made of a divinyl ether functionalized urethane based on, for example, a diisocyanate and hydroxybutyl or hydroxyethyl vinyl ether.

[0044] Suitable crosslinking agent having (meth)acrylic groups include for example dimethacrylate functionalized urethane based on, for example, a diisocyanate and hydroxyethyl methacrylate or polymethacrylate functionalised urethanes.

[0045] Suitable difunctional isocyanates used in the preparation of the crosslinking agent include isophorone diisocyanate, or methylene diisocyanate, or methylenebiscyclohexylisocyanate. Functionalized oligomers derived from these diisocyanates such as isocyanurates, uretdiones, and biurets can, for example, also be used.

[0046] Preparation of vinyl ether functionalized diurethanes can be carried out by means of the process described in, for example, EP-A-505 803.

[0047] Preparation of suitable vinyl ether terminated ester oligomers for use as crosslinking agent is described in WO-A-89/10.346, the complete disclosure of which is incorporated herein by reference. A suitable vinyl ester functional compound is, for example, divinyl adipate.

[0048] The crosslinking agent preferably contains between about 1 to 10 vinyl groups, and more preferably, contains at least two vinyl groups per molecule.

[0049] The crosslinking agent can be a liquid or a solid. Solid crosslinking agents are preferred because good powder stability is more easily achieved, after combination of the crosslinking agent with the unsaturated polymer.

[0050] The crosslinker having allyl groups can for example have 2-12 allyl groups. The crosslinker can have allylether groups and further ester or urethane groups. The crosslinker can also have vinyl ether and allylether groups. It is also possible to use vinyl ether and allylether containing crosslinkers.

[0051] Very suitable crosslinkers include, for example, the ester of trimethylolpropane diallyl ether or pentaerythritol triallyl ether and a polycarboxylic acid (anhydride). Also oligomers containing allyl groups, for example, allyl alcohol, trimethylolpropane diallyl ether, allyl glycidyl ethers and pentaerythritol triallyl ether. Examples of suitable isocyanates are isophorone diisocyanate, toluene diisocyanate, hexamethylene diisocyanate and methylene biscyclohexylisocyanate.

[0052] The relative amounts of polymer having unsaturated groups and crosslinking agent in the binder composition depend in part on the choice of crosslinking agent. In general, if the crosslinking agent is vinyl ether functionalized, the equivalent ratio of polymer unsaturation to crosslinking agent unsaturation is between 1:2 and about 2:1, and preferably, about 1:1. In general, if the crosslinking agent is a methacrylate or a vinyl ester functionalized compound, the equivalent ratio of polymer unsaturation to crosslinking agent unsaturation is between about 1:2 and about 2:1, and preferably, about 1:1.3.

[0053] A suitable cationic curable system based on epoxy resins is disclosed in EP-A-667381.

[0054] Radiation curing is preferably carried out via ultraviolet (UV) or electron beam (EB) curing. These techniques are described in, for example, the article, "UV and EB-curing", by S.J. Bett et al. in Jocca 1990 (11), pgs. 446-453.

Most preferably UV-curing is applied. Very suitable UV-lamps for curing thin layers or to obtain high speeds are excimer lamps (as described for example at pages 48-52 of the Conference Proceedings of RAD TECH Europe September 25, 1995, in Maastricht).

[0055] For UV-radiation curing of the powder paint formulation a photoinitiator is mixed with the binder composition at a temperature between, for example, about 50°C and about 150°C. Mixing can take place in a solvent or in the melt with use of an extruder, wherein the latter is preferred. Pigments, flow promoters, other additives, or mixtures thereof, can also be used.

[0056] Another advantage of the present invention is the fast cure at lower temperatures, in comparison with the prior art processes related to thermocuring systems, resulting in a lower thermal load on the substrate which is very relevant for the present substrates.

[0057] An important advantage of the radiation curing according to the present invention is that flow of the powder paint on exposure to heat is fully separated from the curing reaction on exposure to UV or electron beam radiation, which enables powder coatings to be made that exhibit excellent flow.

[0058] Common additives such as, for example, pigments, fillers, flow promoters, tribo additives, stabilizers, or mixtures thereof can be added to the binder system. Suitable pigments include, for example, inorganic pigments such as titanium dioxide, zinc sulphide or iron and chromium oxide, and organic pigments such as, for example, azo compounds.

[0059] Suitable fillers include, for example, metal oxides, silicates, carbonates, sulfates, or mixtures thereof, as known to those skilled in the art.

[0060] The powder paint compositions can, for example, be prepared and characterized as described in, for example, the aforementioned Misev on pages 224-283. The selection of grinding, classifying and sieving equipment is important for obtaining the desired particle size of the powder paint particles. For this purpose target mills, fluidised bed mills, static classifiers and rotating classifiers may be used.

[0061] Upon curing or fusing of a powder paint composition a powder coating is obtained.

[0062] The median particle size (by volume) of the powder paint particles $X_{50,3}$ (as defined according to the description and notation at pages 12-14 of Mechanische Verfahrenstechnik by Prof. Rumpf (Carl Hansen Verlag, 1975)) can be, for example, below about 200 μm , and preferably, is between about 5 and about 60 μm .

[0063] The selection of the particle size depends on, for example, the desired final coating thickness for a given application.

[0064] The particle size distribution can be as broad as it is in conventional powder paint technology.

[0065] Preferably, the particle size distribution is relatively narrow. More preferably, the ratio $X_{75,3}:X_{25,3} < 3$ (according to the definition in the aforementioned Rumpf), since the efficiency of the development step may vary with the particle size.

[0066] It is one of the advantages of the process according to the present invention, that it is possible to apply particles having median particle sizes between about 5-30 μm . These particle sizes are very suitable to be applied for a clear varnish. It is very difficult to apply particles of such a size with conventional spray guns.

[0067] Carrier particles can be either magnetic or non-magnetic. Preferably, the carrier particles are magnetic particles.

[0068] Suitable magnetic carrier particles have a core of, for example, iron, steel, nickel, magnetite, $\gamma\text{-Fe}_2\text{O}_3$, or certain ferrites such as for example CuZn, NiZn, MnZn and barium ferrites. These particles can be of various shapes, for example, irregular or regular shape.

[0069] Generally, these carrier particles have a median particle size between 20 and 700 μm . Preferably, the carrier particle size distribution is narrow and more preferably the ratio $X_{75,3}:X_{25,3} < 2$.

[0070] Exemplary non-magnetic carrier particles include glass, non-magnetic metal, polymer and ceramic material.

[0071] Non-magnetic and magnetic carrier particles can have similar particle size.

[0072] Preferably the carrier core particles are coated or surface treated with diverse organic or inorganic materials to obtain, for example, desirable electrical, triboelectrical and/or mechanical properties. Inorganic materials are described in for example US-A-4925762 and US-A-5039587. Organic coating materials include, for example, polymers having fluor-, silicone-, acrylic-, styrene-acrylic, melamine- or urethane-group. Mixtures of these polymers can also be used. Preferably a fluor containing polymer is used as coating.

[0073] For coating the carrier particles, any suitable method to coat a thin or thick layer on a powder surface, such as, for example spray coating in a fluidized bed or dry coating in a rotary kiln, can be used.

[0074] The carrier coatings can comprise suitable fillers or additives to control for example, triboelectrical, electrical or mechanical properties of the carrier coating. For example, conductive materials such as, carbon black and metals powder, or charge controlling material and flow improving materials can be used.

[0075] The carrier particles may be conductive (as described in for example US-A-4076857) or non-conductive.

[0076] Preferably, carrier particles having high voltage break through are used so that high electric fields can be used between the transport means and the substrate or the transfer medium to achieve a thick powder coating layer.

[0077] A developer comprises a mixture of powder paint particles and carrier particles. A development method is a

way of developing and a development unit is a complete system comprising of, for example, a developer roller (transport medium), mixing screw(s), a supply device, blades, detectors and the like. Suitable examples are described in, for example, GB-A-2097701, US-A-4147127 and US-A-4131081.

[0078] In the present invention the development method can be either one-component or two-component. According to a preferred embodiment of the invention the two-component development method, in which the carrier particles are mixed with the powder paint particles, is used. Alternatively, also all kinds of monocomponent development like, for example, magnetic conductive, magnetic insulative or non magnetic development as disclosed on pages 203 ff of the above mentioned Schein or binary developers consisting of e.g. magnetic toner and carrier as described in US-A-5516613 can be used.

[0079] Preferably, a combination of powder paint particles having a $X_{50,3}$ below $80\ \mu\text{m}$ and a $X_{95,3}$ below $120\ \mu\text{m}$ and carrier particles having a $X_{50,3}$ below $180\ \mu\text{m}$ and a $X_{95,3}$ below $200\ \mu\text{m}$ is used.

[0080] More preferably, a combination of powder paint particles having a $X_{50,3}$ below $30\ \mu\text{m}$ and above $5\ \mu\text{m}$ and a $X_{95,3}$ below $50\ \mu\text{m}$ and carrier particles having a $X_{50,3}$ below $180\ \mu\text{m}$ and above $5\ \mu\text{m}$ and a $X_{95,3}$ below $200\ \mu\text{m}$ is used.

[0081] In the two-component developer the amount of powder paint particles can be, for example, between about 1 and about 50 wt.% and preferably between about 5 and about 25 wt.% (relative to the amount of developer). It is an advantage of the process according to the invention that it is possible to use powder paint concentrations well in excess of 10 wt.%, which is usually not possible in printing applications. Consequently, the amount of carrier particles can be between about 50 and about 99% by weight (relative to the amount of developer) and preferably is between about 75 wt.% and about 95 wt.%.

[0082] The powder paint concentration can be externally or internally (in the development unit) controlled. External control can be effected by measurement of layer thickness of uncured or cured powder by, for example, optical, photothermal or dielectrical means. Internal control can be carried out in the developer station by means of powder paint concentration control by any suitable means like inductive control (see, for example, US-A-4147127 and US-A-4131081) or volume control.

[0083] In a two-component development method the powder paint particles are triboelectrically charged by intensive mixing and friction with the carrier particles.

[0084] In the process according to the present invention it is also possible to use a one component development method with the carrier particles being incorporated in the powder paint particles as disclosed in, for example, US-A-4803143 and US-A-4543312.

[0085] In a one-component development method the particles are charged by induction or friction, depending on the selection of the powder paint particles.

[0086] Both one- and two-component developers can be transported by magnetic, electric and/or mechanical transport.

[0087] Preferably, the means of transport is a conveying method.

[0088] The mixture is preferably conveyed by means of a magnetic roller as described in for example US-A-4460266. In addition to a magnetic brush apparatus also useful in the present process are, for example, non-magnetic cascade development (see page 94 of the hereinbefore incorporated reference of L.B. Schein) and magnetic cascade development (as described in for example "The 9th International Congress on Advances in Non-Impact Printing Technologies/Japan Hardcopy '93, pages 133-140). In addition also transport by air, for example, powder cloud development can be used. An exemplary process is described in for example US-A-2725304. Also jumping (projection) development (see for example Electrophotography, Fourth International Conference, pages 207-228, Nov. 16-18, 1981) can be carried out.

[0089] When two-component developers are used, the parameters which are relevant for the process (such as, for example, powder paint concentration, development potential and machine parameters) can be chosen depending on the application. This may lead to batch developer replacement, e.g. after certain time intervals or if certain parameters are out of a control range. Preferably, continuous developer material replenishment, as described in, for example, US-A-4614165, can be used to avoid process interruption for batch replenishment.

[0090] The substrate can have any desired shape such as band or sheet, i.e. continuous or discontinuous.

[0091] If a transfer medium is used between the transport means and the substrate any suitable transfer medium like, for example, metallic drums, dielectric drums, foil from metals or polymers like silicone rubber, as described in "Proceeding of IS&T's Seventh International Congress on Advances in Non Impact Printing Technologies", Vol. II, page 453-462, a web as disclosed in EP-A-332223, or composite materials can be used.

[0092] Alternatively a two step transfer may be used in which a layer of powder paint is developed on a first transfer medium and then transferred to a second transfer medium and finally transferred to the substrate.

[0093] The present coating process can be advantageously used in the application of varnishes. Surprisingly, it was found that fully closed layers having a thickness of about $5\ \mu\text{m}$ can easily be obtained with the process according to the invention whereas it is very difficult to obtain such layers with spraying techniques.

[0094] Generally, more layers can be applied with or without intermediate fusing separately on the substrate or sep-

arately on the transfer medium and jointly transferred to the substrate.

[0095] A preferred process according to the present invention thus comprises charging of the powder paint particles by intensive mixing and friction with magnetic carrier particles, transport of carrier particles and powder paint particles with the aid of a magnetic roller and subsequent application of the powder paint particles to a substrate or a transfer medium, and subsequently transferred to the substrate, by means of an electric field between the substrate or the transfer medium and the magnetic roller, whereafter the powder paint composition is cured or fused to a powder coating using techniques known in the art.

[0096] For melting, the applied powder paint can be transferred into an oven or can be exposed to IR radiation, or a combination of both. Alternatively all other suitable fusing methods e.g. as disclosed on page 47-49 of the above mentioned Schein can be used. The applied powder paint is molten at temperatures between, for example, about 60°C and about 140°C to form a continuous, smooth, softened or molten coating with coating thickness between, for example, about 1 µm and about 100 µm. Then, the hot panel is cured with use of a UV light source. Post-heating can also be carried out. The powder coating adheres to the substrate.

[0097] It is possible to apply the coating on printed substrates produced with common printing techniques (offset, gravure, flexo, digital printing either electrographic or inkjet). The printing process and the coating process can be carried out in two separate steps (off-line) or as well in one production step (on-line).

[0098] The coating may cover the full area of the substrate or only part of it (spot coating). In case of spot coating any image creating technology as described in the above mentioned Schein may be used to create an image on a suitable transfer medium or as first transfer medium in case of two step transfer as described before.

[0099] The carrier particles may be metered to a mixing arrangement in which, one or more means of intensive mixing such as, for example, worm wheels are present along with a magnetic roller. Suitable mixing arrangements are described in, for example, "Proceeding of IS&T's Seventh International Congress on "Advances in Non Impact Printing Technologies", Vol. 1, pages 259-265.

[0100] Next, an amount of powder paint particle is fed into the mixing arrangement which is selected so as to obtain a powder paint particles concentration of, for example, about 5-25 wt. % powder paint relative to the amount of carrier particles. In this way, a developer is formed.

[0101] During the intensive mixing and friction in the mixing arrangement, due to the action of the worm weels, the carrier particles and the powder paint particles become oppositely (tribo) electrically charged. A layer of electrically charged powder paint particles covers the carrier particles. The carrier particles subsequently act as carrier for the charged powder paint particles. Next, the developer is fed to the magnetic roller, on which a brush-like structure, also known as the magnetic brush, is formed. The magnetic roller transports the brush to the contact area with the substrate or transfer medium. In this way, powder paint particles, as well as carrier particles, become available at the contact area with the substrate or transfer medium. By applying a sufficiently strong electric field between the magnetic roller and the substrate or transfer medium the powder paint particles can be drawn from the brush to the substrate or transfer medium, onto which they adhere electrostatically. In the case a transfer medium is used, the powder paint particles are subsequently transported to the contact area of the transfer medium and the substrate and next transferred to the substrate by means of one of the aforementioned transfer processes.

[0102] Finally, the magnetic brush is scraped off the magnetic roller as it is returned into the mixing bin.

[0103] As a result, a layer of powder paint particles forms on the substrate, which layer is substantially free from carrier particles, and can then be cured. Eventually, an apparatus which can catch carrier particles can be introduced such as for example a catching equipment for residual carrier, as described in "Proceeding of IS&T Eighth International Congress on Advances in Non Impact Printing Technologies", pages 391-393. The thickness of said layer of powder paint particles can, for example, be controlled via the electric field strength between the magnetic roller and the substrate, or the transfer medium, the magnitude of the charge on the powder paint particles (e.g. by varying the concentration and the mixing time) and the roller speed.

[0104] The process according to the invention can advantageously be applied in equipment for small-scale application of overprint varnishes. These machines can be used online or offline in connection with black and white, two colour or full colour copy machines or computer output printers to produce paper or cardboard sheets with high gloss and high resistance e.g. against fingerprints, oil and acids. The process may be used as an alternative to lamination.

[0105] The process can also be used in-line or off-line in connection with printing machines of any speed and any technology (for example large scale) like offset, gravure, flexo or digital printing to produce overprint varnishes e.g. for cover sheets of booklets and printed cardboard for packaging.

[0106] The process may be used for varnishes, which may be applied below or above a tonerbased image to improve adhesion of the toner to the paper and to improve protection against, for instance, falsification of a document.

[0107] The development station with toner hopper and optional the transfer means and the fusing and curing means may be designed in a way that it can be easily interchanged, for instance as a cartridge, by any (unskilled) person, for example, for use in a copying machine or laser printer. Consequently, these small scale overprint varnish application machines can be used, for example, in printing shops, copy shops and offices.

[0108] The article "An electrostatic process for applying dry coatings on paper" by Reif (TAPPI, October 1955, Vol 38, no 10, pages 607-609) discloses an electrostatic process for applying dry coatings on paper. The applied coating unit and process are different from the present application because amongst others the coating material is suspended as a dust cloud in air, the charging is carried out with a corona discharge, the powder paint particles are not charged in the presence of magnetic or non-magnetic particles and there is no reference to a radiation curable binder system.

[0109] The invention will be further described based on the following non-limiting examples.

Examples

Example I

Preparation of powder paint composition I

[0110] A powder paint composition was prepared by premixing 830 parts by weight of a polyester resin (Uralac XP3125 of DSM Resins), 170 parts by weight of a crosslinker (Uralac ZW 3307 of DSM Resins), 10 parts by weight of photoinitiator (Irgacure 184™) and 6 parts by weight of flow agent (Byk 361™) in a Henschel batch mixer and next melt kneaded in a Buss-Ko-Kneader PLK 46.

[0111] The cooled extrudate was milled first in a hammer mill to a particle size < 3mm and then fed into a target mill (NPK Labojet) obtaining a powder paint with a medium particle size of 10.8 μm and a $d_{75,3}/d_{25,3}$ ratio of 3.3.

Example II

Preparation of a carrier

[0112] 998 parts by weight Cu-Zn-ferrite powder, having a median particle size of 81 μm and a ratio $X_{75,3}/X_{25,3}$ of 1,32 (both measured with the laser granulometer Cilas HR 850), were dry coated with 2 parts by weight polyvinylidenedifluoride (Kynar 301F™) by mixing both materials in a Lödige mixer and coating the polymer on the surface of the ferrite in a rotary kiln at 200°C under N₂-atmosphere to obtain a carrier with a medium size of 80 μm, a ratio $X_{75,3}/X_{25,3}$ of 1.32, a resistance of $1.1 \cdot 10^{10}$ Ohm at a potential of 10V and a break-through voltage above 1,000V (both measured in a c-meter of Epping GmbH).

Example III

Preparation of developer I

[0113] 16% by weight of the powder paint composition according to Example I and 84% by weight of the carrier according to Example II were mixed at room temperature intensively in a "Skandex" paint shaker for 5 minutes to obtain a developer. The charge distribution of the developer was measured in a q-meter of Epping GmbH showing a narrow charge over diameter (q/d)-distribution with a median of 2.2 fC/10 μm, a standard deviation of 1.7 fC/10 μm and 5.2% oppositely charged particles.

Example IV

Coating on a substrate

[0114] The developer according to Example III was filled in a magnetic brush unit mounted in a distance of 2.5 mm of a rotating metal drum available as the Id-tester (developer life time tester) from Epping GmbH. On the rotating drum a cardboard substrate of 0.3 mm thickness preprinted with red offset printing ink was mounted. The rotation speed of the drum (i.e. coating speed) was 30 m/minute, and the speed of the magnetic brush was 78 meters/minute in the same direction as the drum. The doctor blade of the magnetic brush was adjusted to a distance of 1.5 mm to the magnetic roller. The magnetic pole was adjusted -10 degrees compared to the line between both rotating axes. The development potential of the drum against the developer roller was set to the following values (Table I):

TABLE I

development voltage	average coating layer thickness	coating properties
-1000 V	7.5 μm	high gloss (97%), closed film, oil-and-tensid tight

TABLE I (continued)

development voltage	average coating layer thickness	coating properties
-800 V	3.5 μm	high gloss (94%), closed film, oil-and tensid tight
-600 V	2.5 μm	medium gloss (75%)
-400 V	1.5 μm	low gloss (38%)
-200 V	1 μm	slight gloss (19%)

After application on the cardboard substrate, the powder was heated at 70°C by means of IR to obtain a good flowing film, followed by a UV radiation treatment (1000mJ/cm²). The result in the examples of the first two blocks of Table I is a chemical resistant, hard and scratch resistant coating.

[0115] The gloss was measured with a Reflectometer supplied by Dr. Lange at 60° detection angle (according to DIN 67530).

Example V

Preparation of powder paint II

[0116] 99.5 parts by weight of the powder paint composition of Example I were mixed with 0.5 parts of weight of siliciumdioxide (Aerosil R504™) in a Henschel batch mixer at maximum speed for 3 minutes to achieve a powder paint II with excellent powder flow behaviour.

Example VI

Preparation of powder paint III

[0117] 99.5 parts by weight of the powder paint composition of Example I were mixed with 0.5 parts of weight of titaniumdioxide (Aerosil P25™) in a Henschel batch mixer at maximum speed for 3 minutes to achieve powder paint III with excellent powder flow behaviour.

Example VII

Preparation of developer II

[0118] 11 parts by weight of the powder paint composition II according to Example V and 89 parts by weight of the carrier according to Example II were mixed in a "Skandex" paint shaker for 5 minutes to obtain a non-dusting developer II.

Example VIII

Preparation of developer III

[0119] 15 parts by weight of the powder paint composition III according to Example VI and 85% by weight of the carrier according to example II were mixed in a "Skandex" paint shaker for 5 minutes to obtain a non-dusting developer III.

Example IX

Coating a substrate

[0120] Analogous to Example IV the developer II according to Example VII and the developer III according Example VIII were used to produce a chemical resistant, hard and scratch resistant coating on 0.3 mm thick cardboard preprinted with red offset ink (see Table II).

TABLE II

	development voltage	average coating layer thickness	coating properties	
5	developer II	-1000V	7.6 μm	medium gloss (55-60%), closed film, oil and tensid tight
	developer III	-1000V	9.7 μm	high gloss (80-85%), closed film, oil and tensid tight

10 Example X

Preparation of a powderpaint IV

15 **[0121]** The cooled extrudate from Example I was milled first in a hammer mill to a particle size <3 mm and then fed into a fluidized bed mill (Condux CFS8), having a nozzle diameter of 4 mm. The material was milled with 6 bar over-pressure at 3800 r.p.m. of the classifier wheel incorporated in the mill and after that fed into a separate classifier (Condux CGS16) at 8000 r.p.m. of the classifier wheel to reduce the fraction of fine particles below 5 μm in the powder obtaining a powder with a median particle size of 13.7 μm and a ratio $X_{75.3}/X_{25.3}$ ratio of 2.3. 99.5 parts by weight of this powder were mixed with 0.5 parts of weight of titaniumdioxide (Aerosil P25™) in a Henschel batch mixer at maximum speed for 3 minutes to achieve powder paint IV with excellent powder flow behaviour.

20 Example XI

Preparation of developer IV

25 **[0122]** 10 parts by weight of the powder paint according to Example X and 90% by weight of the carrier according to example II were mixed in a "Skandex" paint shaker for 5 minutes to obtain a non-dusting developer IV.

30 Example XII

Coating a substrate

35 **[0123]** Analogous to example IX the developer IV according to Example XI was used to produce a 7.5 μm thick coating on a 90 g/m² paper preprinted in a commercially available dry toner based 4 colour copier/printer. The coating was proven to be hard and chemical, scratch and fingerprint resistant. The coated sheets were medium glossy (60-70%). The protection of prints against falsification were improved as any damage of the surface can easily be detected by the change of gloss of the surface.

40 **Claims**

- 45 **1.** A process for coating a board- or paper-like substrate with a powder paint composition, characterized in that powder paint particles are first charged by friction or induction in the presence of magnetic or non-magnetic particles, are next transported and are then applied to the substrate or applied to a transfer medium, and are then subsequently transferred to the substrate, by means of an electric field between the substrate respectively the transfer medium and the means of transport, whereafter the powder paint composition is fused and cured to a powder coating wherein the powder paint particles are based on solid particles of a radiation curable binder.
- 50 **2.** A process according to Claim 1 characterised in that the radiation curable binder comprises a polymer having unsaturated groups.
- 3.** A process according to any one of Claims 1-2, characterized in that the substrate is cardboard, hardboard, fibre board, particle board, chip board, plywood, veneer, block board, wood, timber or paper.
- 55 **4.** A process according to any of Claims 1-3, characterized in that the substrate is cardboard or paper.

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5. A process according to any one Claims 1-4, characterized in that the powder paint particles are mixed with magnetic or non-magnetic carrier particles to obtain friction charging whereupon the mixture is transported and the powder paint particles are applied to the substrate by means of an electric field between the substrate and the means of transport.
 6. A process according to any one of Claims 1-5, characterized in that the powder paint particles have a $X_{50,3}$ below 80 μm and a $X_{95,3}$ below 120 μm .
 7. A process according to any one of Claims 1-6, characterized in that the powder paint particles have a $X_{50,3}$ below 30 μm and above 5 μm and a $X_{95,3}$ below 50 μm .
 8. A process according to any one of Claims 1-7, characterized in that the carrier particles have a $X_{50,3}$ below 180 μm and above 5 μm and a $X_{95,3}$ below 200 μm .
 9. A process according to any one of Claims 1-8, characterized in that the magnetic or non-magnetic carrier particles are selected from magnetic carrier particles consisting of a core of iron, steel, nickel, magnetite, $\gamma\text{-Fe}_2\text{O}_3$ or ferrites or non-magnetic carrier particles including glass, non-magnetic metal, polymer and ceramic material.
 10. A process according to any one of Claims 1-9, characterized in that the process comprises charging of the powder paint particles by intensive mixing and friction with magnetic carrier particles, transport of carrier particles and powder paint particles with the aid of a magnetic roller and subsequent application of the powder paint particles to the substrate or to a transfer medium by means of an electric field between the substrate and the magnetic roller, whereafter the powder paint composition is cured or fused to a powder coating.
 11. Use of a process according to any one of Claims 1-10 in the application of overprint varnishes.
 12. Coated board- or paper-like substrate wherein the coating is obtainable by a process according to any one of Claims 1-10.

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Patentansprüche

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1. Verfahren zum Beschichten eines karton- oder papierähnlichen Substrats mit einer Pulverlackzusammensetzung, dadurch gekennzeichnet, daß Pulverlackteilchen zuerst durch Reibung oder Induktion in Gegenwart von magnetischen oder nicht-magnetischen Teilchen aufgeladen werden, als nächstes transportiert werden und dann auf das Substrat aufgetragen werden oder auf ein Transfermedium aufgetragen werden und darauffolgend auf das Substrat übertragen werden, mittels eines elektrischen Felds zwischen dem Substrat bzw. dem Transfermedium und dem Transportmittel, woraufhin die Pulverlackzusammensetzung zu einem Pulverüberzug geschmolzen und gehärtet wird, wobei die Pulverlackteilchen auf festen Teilchen eines strahlungshärtbaren Bindemittels basieren.
 2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das strahlungshärtbare Bindungsmittel ein Polymer mit ungesättigten Gruppen umfaßt.
 3. Verfahren nach irgendeinem der Ansprüche 1 bis 2, dadurch gekennzeichnet, daß das Substrat Karton, Hartplatte, Faserplatte, Spanplatte, Graupappe, Sperrholz, Furnier, Tischlerplatte, Holz, Bauholz oder Papier ist.
 4. Verfahren nach irgendeinem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das Substrat Karton oder Papier ist.
 5. Verfahren nach irgendeinem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß die Pulverlackteilchen mit magnetischen oder nicht-magnetischen Trägerteilchen gemischt werden, um Aufladen durch Reibung zu erhalten, woraufhin die Mischung transportiert wird und die Pulverlackteilchen auf das Substrat mittels eines elektrischen Felds zwischen dem Substrat und dem Transportmittel aufgetragen werden.
 6. Verfahren nach irgendeinem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die Pulverlackteilchen einen $X_{50,3}$ -Wert unter 80 μm und einen $X_{95,3}$ -Wert unter 120 μm aufweisen.
 7. Verfahren nach irgendeinem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß die Pulverlackteilchen einen

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$X_{50,3}$ -Wert unter $30\ \mu\text{m}$ und über $5\ \mu\text{m}$ und einen $X_{95,3}$ -Wert unter $50\ \mu\text{m}$ aufweisen.

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8. Verfahren nach irgendeinem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß die Trägerteilchen einen $X_{50,3}$ -Wert unter $180\ \mu\text{m}$ und über $5\ \mu\text{m}$ und einen $X_{95,3}$ -Wert unter $200\ \mu\text{m}$ aufweisen.
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9. Verfahren nach irgendeinem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß die magnetischen oder nicht-magnetischen Trägerteilchen aus magnetischen Trägerteilchen, welche aus einem Kern aus Eisen, Stahl, Nickel, Magnetit, $\gamma\text{-Fe}_2\text{O}_3$ oder Ferriten bestehen, oder nicht-magnetischen Trägerteilchen, welche Glas, nicht-magnetisches Metall, Polymer und keramisches Material einschließen, ausgewählt werden.
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10. Verfahren nach irgendeinem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß das Verfahren das Aufladen der Pulverlackteilchen durch intensives Mischen und Reibung mit magnetischen Trägerteilchen, den Transport von Trägerteilchen und Pulverlackteilchen mit Hilfe einer magnetischen Druckwalze und das darauffolgende Auftragen der Pulverlackteilchen auf das Substrat oder auf ein Transfermittel mittels eines elektrischen Felds zwischen dem Substrat und der magnetischen Druckwalze, woraufhin die Pulverlackzusammensetzung zu einem Pulverüberzug gehärtet oder geschmolzen wird, umfaßt.
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11. Verwendung eines Verfahrens nach irgendeinem der Ansprüche 1 bis 10 beim Auftragen von Aufdrucklacken.
12. Beschichtetes karton- oder papierartiges Substrat, wobei der Überzug durch ein Verfahren gemäß irgendeinem der Ansprüche 1 bis 10 erhältlich ist.

Revendications

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1. Un procédé pour l'enduction d'un substrat de type carton ou papier avec une composition de peinture en poudre, caractérisé en ce que les particules de peinture en poudre sont d'abord chargées par frottement ou induction en présence de particules magnétiques ou non-magnétiques, sont ensuite transportées et sont alors appliquées au substrat ou sont appliquées sur un milieu de transfert, et sont alors, par la suite transférées sur un substrat, au moyen d'un champ électrique entre le substrat, respectivement le milieu de transfert et le moyen de transport, après quoi la composition de peinture en poudre est fondue puis réticulée en une enduction en poudre, dans laquelle les particules de peinture en poudre sont à base de particules solides d'un agent liant réticulable par radiation.
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2. Un procédé selon la revendication 1, caractérisé en ce que l'agent liant réticulable par radiation comporte un polymère ayant des groupes insaturés.
3. Un procédé selon l'une quelconque des revendications 1 et 2, caractérisé en ce que le substrat est du carton, du panneau dur, du panneau en fibres, du panneau en particules, du panneau en copeaux, du contre-plaqué, de la feuille de placage, du panneau latté, du bois, du bois de construction ou du papier.
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4. Un procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que le substrat est du carton ou du papier.
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5. Un procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que les particules de peinture en poudre sont mélangées avec des particules supports, magnétiques ou non-magnétiques, afin d'obtenir une charge par frottement, après quoi le mélange est transporté et le mélange de particules en poudre est appliqué sur le substrat au moyen d'un champ électrique entre le substrat et le moyen de transport.
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6. Un procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce que les particules de peinture en poudre ont un $X_{50,3}$ inférieur à $80\ \mu\text{m}$ ou bien $X_{95,3}$ inférieur à $120\ \mu\text{m}$.
7. Un procédé selon l'une quelconque des revendications 1 à 6, caractérisé en ce que les particules de peinture en poudre ont un $X_{50,3}$ inférieur à $30\ \mu\text{m}$ et supérieur à $5\ \mu\text{m}$ et un $X_{95,3}$ inférieur $50\ \mu\text{m}$.
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8. Un procédé selon l'une quelconque des revendications 1 à 7, caractérisé en ce que les particules supports ont un $X_{50,3}$ inférieur à $180\ \mu\text{m}$ et supérieur à $5\ \mu\text{m}$ et un $X_{95,3}$ inférieur à $200\ \mu\text{m}$.

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9. Un procédé selon l'une quelconque des revendications 1 à 8, caractérisé en ce que les particules supports, magnétiques ou non-magnétiques, sont choisies parmi les particules supports magnétiques constituées d'une âme en fer, en acier, en nickel, en magnétite, en $\gamma\text{-Fe}_2\text{O}_3$ ou en ferrites ou bien des particules supports non-magnétiques comportant du verre, un métal non-magnétique, un polymère et un matériau céramique.

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10. Un procédé selon l'une quelconque des revendications 1 à 9, caractérisé en ce que le procédé consiste à charger des particules de peinture en poudre par mélange et frottement intensifs avec des particules supports magnétiques, à transporter des particules supports et des particules de peinture en poudre à l'aide d'un cylindre magnétique et à appliquer par la suite des particules de peinture en poudre sur le substrat ou sur un milieu de transfert au moyen d'un champ électrique entre le substrat et le cylindre magnétique, après quoi la composition de peinture en poudre est réticulée ou fondue en une enduction en poudre.

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11. Utilisation d'un procédé selon l'une quelconque des revendications 1 à 10, dans l'application de vernis de surimpression.

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12. Substrat enduit de type carton ou papier dans lequel l'enduction peut être obtenue au moyen d'un procédé selon l'une quelconque des revendications 1 à 10.

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