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METHOD OF ELECTROSTATIC PRINTING

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ABSTRACT OF THE DISCLOSURE

In a method of powder electrostatic printing wherein the powder particles comprise a dispersion of (1) a continuous resinous phase which comprises at least one member of the group consisting of limed rosin, cyclized rubber, copolymers of alpha-methyl styrene and vinyl toluene, pentaerythritol esters of rosin and polyterpene resins, and a dispersed phase comprising (2) a pigment and (3) particle interpolymers derived from latices.

This invention relates to electrostatic printing and copying methods which involve applying charged powder particles to a substrate bearing an opposite charge. More particularly this invention provides a method of printing electrostatically which may be used on surfaces of materials which are especially difficult to print upon such as polyolefins and rubber.

The method of this invention is applicable to virtually all systems of electrostatic printing or copying which employ powder to print or develop their images. The method may be used in electrostatic system in which the powder is applied in an overall manner to an electrostatic charge pattern on a surface, the powder only adhering to the charged areas to convert the charge pattern into a visible image. Examples of such a system are the conventional electrostatic copying and printing processes described in U.S. Pat. Nos. 2,297,691 and 3,053,539.

Furthermore, the method may be used in systems in which charged particles prearranged into a pattern are applied to a substrate bearing a blanket charge opposite in polarity to that of the particles. These latter systems are of two major types. U.S. Pat. 3,081,698 describes one type wherein the powder particles are charged and prearranged into a pattern by being brushed through a stencil or screen having apertures arranged in the pattern into which the powder particles are to be arranged. The particles which pass through the screen arranged in the pattern are attracted to the charged substrate beyond the screen.

The other type is a system involving gravure printing such as that described in copending application Ser. No. 372,226 filed June 3, 1964 in which powder is formed into a pattern by being deposited into the cells of a gravure plate. The powder is then charged and transferred to the substrate having a blanket charge of opposite polarity.

It is in the systems in which charged particles prearranged into a pattern are applied to a substrate having a blanket charge that the method of this invention is particularly useful because there is a desire to find a practical method for using these systems for printing on such problem materials as polyolefins and rubber.

We have found that by using the powder which we will hereinafter describe in all of the aforementioned electrostatic printing and copying systems in place of the powders or developers used in said systems, we can produce printed matter of excellent flexibility, glass, rub and scratch resistance and of superior adhesion, particularly to problem surfaces such as polyolefins, including

polypropylene and high and low density polyethylene and rubber.

The powder used in the improved method of this invention consists of particles, each of which is a dispersion in (1) a continuous resinous phase which comprises at least one member of the group consisting of limed rosin, cyclized rubber, copolymers of alpha-methyl styrene and vinyl toluene, pentaerythritol esters of rosin and polyterpene resins of (2) pigment and (3) particle interpolymers which form either the particulate phase of the latices described in U.S. Pat. 2,767,153, the particulate phase of latices comprising vinyl acetate polymers of 40–90 parts of vinyl acetate and about 10 to 60 parts of an acrylate selected from the group consisting of n-butyl acrylate and 2-ethylhexyl acrylate or the particulate phase of latices comprising polymers of styrene and butadiene. Components (2) and (3) form the dispersed phases in the particles.

It should be noted that in the specification and claims, all proportions are by weight unless otherwise specified.

The particulate interpolymers of the latices of U.S. Pat. 2,767,153 are described as interpolymers comprising 35–60 parts by weight of an unsaturated ester taken from the group consisting of straight-chain and branched-chain saturated aliphatic alcohol esters of acrylic and methacrylic acids containing a total of about 5–20 carbon atoms in the alcohol radical of which about 5–14 carbon atoms comprise the longest continuous chain thereof, about 3–10 parts by weight of an unsaturated nitrile taken from the group consisting of acrylonitrile and methacrylonitrile about 2–5 parts by weight of an unsaturated monocarboxylic acid taken from the group consisting of acrylic acid, methacrylic acid, cinnamic acid, atropic acid, and crotonic acid and, correspondingly, about 60–25 parts by weight of a monovinylidene aromatic hydrocarbon, the interpolymer particles in said latex having an average diameter of up to 0.5 micron. It has been found that best results are obtained when said interpolymer comprises from 35–45 parts of either ethylhexyl acrylate, decyl acrylate or tridecyl acrylate; 3–10 parts of acrylonitrile, 2–5 parts of methacrylic acid and 60–40 parts of styrene.

The particulate polymers of the vinyl acetate latices are internally plasticized vinyl acetate polymers. Vinyl acetate polymers are plasticized for greater flexibility either "externally" by conventionally blending the polymers with plasticizers or "internally" by copolymerizing the polymers with monomers which will enhance flexibility. The vinyl acetate polymers of this invention are internally plasticized with acrylate monomers, preferably n-butyl acrylate or 2-ethylhexyl acrylate. In addition to the acrylates, the vinyl acetate polymers may further contain small amounts, in order of from 1 to 5%, of conventional internal plasticizers for vinyl acetate such as vinyl stearate, monoisopropyl maleate and diethylmaleate. The vinyl acetate polymers internally plasticized with acrylates may be conveniently made in accordance with the procedure set forth in U.S. Pat. No. 3,057,812, particularly Example 48. The polymer may contain from 10 to 60% of acrylate but most preferably, they contain 10 to 25% of acrylate.

The particulate polymers of styrene and butadiene preferably contain from 10–30% butadiene and from 70%–90% styrene.

Preferably, a waxy material is also dispersed in the continuous resinous phase. The waxy dispersed material may be a low molecular weight waxy polyethylene, e.g., polyethylene having a molecular weight of 40,000 or lower, most preferably from 2500 to 10,000. Polyethylene glycol "waxes" having molecular weights of less than 20,000 as well as polyethylene glycol distearate may also

be used as the waxy dispersed material. The wax also may be paraffin wax, polymekon wax, microcrystalline wax or carnauba wax.

The pigment may be virtually any conventional pigment such as methyl violet, titanium dioxide, cyanine blue, lithol red and carbon black. Any of the pigments conventionally used in electrostatic developers may be used as may most ink pigments.

As for the continuous resinous phase materials, the pentaerythritol esters of rosin are formed by the esterification with pentaerythritol of rosin, polymerized rosin and maleated or fumarated rosin. The polyterpene rosins include both the conventional terpene homopolymers e.g., the polymerization products of beta-pinene as well as the terpene-phenolic copolymers which are the condensation products of polyterpene polymers with phenol-formaldehydes.

The cyclized rubber may be made by any conventional method such as condensing rubber with metallic or metalloid halide catalysts such as stannic chloride, titanium tetrachloride, ferric chloride and antimony pentachloride in a suitable solvent. Upon the treatment of the resultant product with acetone or alcohol, the salt is reformed together with formation of cyclized rubber. Similar results may be obtained following the methods set forth in "The Paper Trade Journal," p. 96, Feb. 23, 1939, "Rubber Age," April 1939, and "Journal of Industrial Engineering Chemistry," XIX, 1033, XXVI, 125 and XXXIII, 389. Details of preparation are also disclosed in U.S. Pat. Nos. 1,797,188, 1,836,247, 1,853,334 and 2,052,931. In addition, limed rosin as well as copolymers of alpha-methyl styrene and vinyl toluene may be used.

Preferably the ratio of the resinous phase to interpolymer in the powder particles is from 0.5:1 to 5:1. Preferably from about up to 0.30 part and most preferably from about 0.15 to 0.25 part of said waxy-material are dispersed for each part of the resinous phase. The pigment is present in conventional proportions, about 1 to 50 parts of pigment present for each part of the remainder of the particles.

While the particles of this invention display excellent adhesion to untreated polypropylene and low density polyethylene rubber, paper and a wide variety of other substrates, the adhesion to high density polyethylene is not up to a par with the adhesion to the polypropylene and low density polyethylene. However, the addition of a small amount of long-chain fatty amides or long-chain fatty acids to the composition brings the adhesion to high density polyethylene up to a par with the adhesion to the other polyolefins. Among the long-chain fatty amides which may be used are octanamide, decanamide, dodecanamide, tetradecanamide, hexadecanamide, octadecanamide, 9–12 octadecadienamide and eicosanamide. Suitable fatty acids for this purpose include stearic acid and oleic acid. When used, the fatty amide or the fatty acid preferably constitutes from 3% to 6% of the weight of the resinous phase.

To prepare powder particles used in this invention, the resin which is to be the continuous phase is mixed with the latex of the polymer which is to be the dispersed phase on milling means to which heat is applicable. The milling means is most conveniently a two-roll mill. The resin is mixed in bulk and undiluted. The latex preferably has a solids content above 35% by weight. As the milling takes place, the mill is heated to about 212° F. or above to evaporate the water from the latex. The milling is conducted at a sufficiently slow rate to assure that substantially all of the water is continuously being driven off. After all of the water is evaporated, the wax and the pigment components are added, and the milling is continued until these are uniformly dispersed in the continuous resin phase, the temperature being maintained at a level sufficient to maintain the mixture in the fluid state. Then the mixture is cooled to room temperature or below. A hard chip forms in the mill. This is removed and broken down to a particle size preferably in the order of from 5–20 microns to provide the powder particles.

The following examples will further illustrate the practice of this invention:

EXAMPLE 1

200 parts of Pentalyn G (the pentaerythritol ester of the maleic adduct of rosin formed by esterifying the reaction product of maleic anhydride and rosin with pentaerythritol, softening point 256°–284° F.) are worked on a two mill at about 260° F. When the Pentalyn G is completely molten, 750 parts of an interpolymer latex having a 40% solids content of an interpolymer of 40% 2-ethylhexyl acrylate, 52% styrene, 6% acrylonitrile and 2% methacrylic acid prepared in accordance with U.S. Pat. 2,767,153—Example 1—are slowly added. During the addition while the working is continued on the mill, the water from the latex evaporates. Milling is continued until substantially all of the water evaporates and a molten plastic mass is in the mill. The mill is allowed to cool and the mass removed as a solid.

Then 76 parts of the above chips are melted on a two-roll mill at about 140° F. 17 parts of methyl violet pigment are added, and the mixture is worked on the mill until the pigment is uniformly dispersed. Then 5 parts of Epolene N–10 (a polyethylene wax having a softening point of 232° F., ring and ball method, a density of 0.927 and a molecular weight of 2500) are added to the mixture and uniformly dispersed therein. The mill is then cooled and the mixture is removed from the mill. The chip is then further broken down on a jet mill to a particle size of 5 to 20 microns.

Using the apparatus of FIG. 2 in U.S. Pat. No. 3,081,698, the mixture is used to print upon a polyethylene substrate. The applied mixture is then fixed to the substrate, as set forth in Pat. No. 3,081,698. The resulting printing displays excellent gloss, excellent rub resistance as well as excellent adhesion to the polyethylene as demonstrated by the standard "Scotch Tape Test." The printed polyethylene also had excellent scratch resistance as demonstrated by scratching the printing using the front part of the nail. The "Scotch Tape Test" is carried out by pressing the adhesive face of Scotch tape against the printing and then jerking the tape away from the printed surface and determining whether any printed material is pulled away by the tape.

It is further noted that if a small amount, about 2 parts of Armid HT, a fatty amide mixture comprising 22% hexadecanamide, 75% octadecanamide and 3% 9-octadecanamide is added at the same time that the polyethylene wax is added, the resulting printing ink displays in addition adhesion and scratch resistance on high density polyethylene which is the equivalent of the excellent adhesion and scratch resistance of printing on low density polyethylene.

The method of this example worked equally well using the gravure electrostatic methods described in copending application Ser. No. 372,226 in which the powder is deposited in the cells of a gravure plate, charged and transferred to a surface having a blanket charge of opposite polarity.

Also, the method of this example worked equally well in the apparatus of U.S. Pat. 3,052,539, an electrostatic copying apparatus, wherein a photoconductive coated sheet is negatively charged, then exposed to a light image leaving a latent electrostatic image. The latent image is developed by applying the powder composition of this example to the latent image and then fixing the powder to the sheet.

The method of this example may be used in electrostatic printing on a wide variety of surfaces including polyethylene, polypropylene, rubber, polystyrene, vinyl and vinylidene chloride polymers and copolymers, cellulose, cellulose acetate, paper, cloth including synthetics such as nylon or Dacron, metal and Mylar (polyethylene terephthalate).

EXAMPLE 2

Example 1 is repeated using the same constituents, proportions and conditions except that in place of the interpolymer latex of Example 1, there is used in interpolymer latex having a 40% solids content of an interpolymer of 40% decyl acrylate, 52% styrene, 6% acrylonitrile and 2% methacrylic acid prepared in accordance with U.S. Pat. 2,767,153 (Example VII). The powder of this example displayed all of the desirable properties of the powder of Example 1 when used in the electrostatic printing and copying methods described in Example 1.

EXAMPLE 3

Example 1 is repeated using the same constituents, proportions and conditions except that in place of the interpolymer latex of Example 1, there is used an interpolymer latex having a 50% solids content of an interpolymer of 40% tridecyl acrylate, 52% styrene, 6% acrylonitrile and 2% methacrylic acid prepared in accordance with U.S. Pat. 2,767,153 (Example VIII). The powder of this example displayed all of the desirable properties of the powder of Example 1 when used in the electrostatic printing and copying methods described in Example 1.

EXAMPLE 4

Example 1 is repeated using the same constituents, proportions and similar conditions except that in place of the Pentalyn G, there is used Picolyte S135 (polyterpene resin homopolymer made by the polymerization of beta-pinene). The powder of this example displayed all of the desirable properties of the powder of Example 1 when used in the electrostatic printing and copying methods described in Example 1.

EXAMPLE 5

Example 1 is repeated using the same constituents, proportions and similar conditions except that in place of the Pentalyn G, there is used Piccotex 120 (copolymer of vinyl toluene and alpha-methyl styrene having an M.P. of 120° C.) The powder of this example displayed all of the desirable properties of the powder of Example 1 when used in the electrostatic printing and copying methods described in Example 1.

EXAMPLE 6

Example 1 is repeated using the same constituents, proportions and similar conditions except that in place of the Pentalyn G, there is used Durez 220 (terpene-phenolic resin, the condensation product of polyterpene with the product of the condensation of phenol and formaldehyde). The powder of this example displayed all of the desirable properties of the powder of Example 1 when used in the electrostatic printing and copying methods described in Example 1.

EXAMPLE 7

Example 1 is repeated using the same constituents, proportions and similar conditions except that in place of the Pentalyn G, there is used Pentalyn K (pentaerythritol ester of dimerized rosin having a softening point of 188–197° C. and a specific gravity of 1.09) in a hydrocarbon solvent having a boiling range of 474–498° F. and a K.B. value of 27–28. The powder of this example displayed all of the desirable properties of the powder of Example 1 when used in the electrostatic printing and copying methods described in Example 1.

EXAMPLE 8

Example 1 is repeated using the same constituents, proportions and similar conditions except that in place of the Pentalyn G, there is used cyclized rubber. The powder of this example displayed all of the desirable properties of the powder of Example 1 when used in the electrostatic printing and copying methods described in Example 1.

EXAMPLE 9

Example 1 is repeated using the same constituents, proportions and similar conditions except that in place of the Pentalyn G, there is used limed rosin, the lime content of which is 6%. The powder of this example displayed all of the desirable properties of the powder of Example 1 when used in the electrostatic printing and copying methods described in Example 1.

EXAMPLE 10

Example 1 is repeated using the same constituents, proportions and similar conditions except that in place of the interpolymer latex, there is used in interpolymer latex having a solids content of 47.7% of an interploymer of 80% vinylacetate, 17% 2-ethylhexyl acrylate and 3% monoisopropyl maleate prepared in accordance with U.S. Pat. No. 3,057,812 (Example 48). The powder of this example displayed all of the desirable properties of the powder of Example 1 when used in the electrostatic printing and copying methods described in Example 1.

EXAMPLE 11

Example 1 is repeated using the same constituents, proportions and similar conditions except that in place of the interpolymer latex, there is used an interpolymer latex having a 50% solids content of an interpolymer comprising 80% vinyl acetate and 20% n-butyl acrylate. The powder of this example displayed all of the desirable properties of the powder of Example 1 when used in the electrostatic printing and copying methods described in Example 1.

EXAMPLE 12

Example 1 is repeated using the same constituents, proportions and similar conditions except that in place of the interpolymer latex, there is used an interpolymer latex having a 40% solids content of an interpolymer comprising 80% styrene and 20% butadiene. The powder of this example displayed all of the desirable properties of the powder of Example 1 when used in the electrostatic printing and copying methods described in Example 1.

EXAMPLE 13

Example 1 is repeated using the same constituents, proportions and similar conditions except that in place of Epolene N–10, there is used a polyethylene wax having a molecular weight of 10,000, a density of 0.947 and a softening point of 259° F. (ring and ball method). The powder of this example displayed all of the desirable properties of the powder of Example 1 when used in the electrostatic printing and copying methods described in Example 1.

The following waxy compositions may be used in Example 1 in place of Epolene N–10 with the same results as in Example 1: polyethylene softening point 106° C. and M.W. 40,000; polyethylene M.W. 1400; Carbowax 6000 (polyethylene glycol having a molecular weight of 6000–7500); Carbowax 20,000 (polyethylene glycol having a molecular weight of 18,000–20,000), the di-stearic acid ester of 6000 molecular weight polyethylene glycol microcrystalline wax, polymekon wax, carnauba wax and paraffin wax.

EXAMPLE 14

The procedure of Example 1 is repeated using the same conditions except that in place of the ingredients, the following ingredients are used:

	Parts
Pentalyn G	32
Interpolymer latex described in Example 1	48
Cyan Blue pigment	20

The resulting powder is successfully used in printing on a paper substrate, an aluminum substrate and a wooden

substrate using both the apparatus of U.S. Pat. No. 3,081,698 as well as the apparatus of U.S. Pat. No. 3,052,539.

While there have been described what is at present considered to be the preferred embodiments of this invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the invention, and it is, therefore, aimed to cover all such changes and modifications as fall within the true spirit and scope of the invention.

I claim:

1. In the method of electrostatic printing on polyolefin substrates and rubber substrates wherein electrostatically charged powder particles are applied to the substrate bearing an opposite electrostatic charge, the improvement which comprises using as the powder, particles which comprise:

(A) a dispersion of a particulate interpolymer selected from the group consisting of (1) polymers of about 35–60 parts by weight of an unsaturated ester taken from the group consisting of straight-chain and branched-chain saturated aliphatic alcohol esters of acrylic and methacrylic acid containing a total of about 5–20 carbon atoms in the alcohol radical of which about 5–14 carbon atoms comprise the longest continuous chain thereof, about 3–10 parts by weight of an unsaturated nitrile taken from the group consisting of acrylonitrile and methacrylonitrile, about 2–5 parts by weight of an unsaturated monocarboxylic acid taken from the group consisting of acrylic acid, methacrylic acid, cinnamic acid, atropic acid and crotonic acid and, correspondingly, about 60–25 parts by weight of a monovinylidene aromatic hydrocarbon, the particles of said interpolymer having an average diameter of up to 0.5 micron, (2) polymers of about 40–90 parts of vinyl acetate and about 10 to 60 parts of an acrylate selected from the group consisting of n-butyl acrylate and 2-ethylhexyl acrylate and (3) polymers of 10 to 30 parts of butadiene and 70 to 90 parts of styrene and

(B) a dispersion of pigments in

(C) a resin selected from the group consisting of limed rosin, pentaerythritol esters of rosin, cyclized rubber, copolymers of alphamethyl styrene and vinyl toluene and polyterpene resins.

2. The method of claim 1 wherein the powder particles further include a waxy material also dispersed in the resin.

3. The method of claim 2 wherein the waxy material is a wax selected from the group consisting of polyethylene having a maximum molecular weight of about 40,000, polyethylene glycol having a maximum molecular weight of 20,000 and polyethylene glycol distearate.

4. The method of claim 3 wherein said interpolymer is a polymer of about 35–60 parts by weight of an unsaturated ester taken from the group consisting of straight-chain and branched-chain saturated aliphatic alcohol esters of acrylic and methacrylic acid containing a total of about 5–20 carbon atoms in the alcohol radical of which about 5–14 carbon atoms comprise the longest continuous chain thereof, about 3–10 parts by weight of an unsaturated nitrile taken from the group consisting of acrylonitrile and methacrylonitrile, about 2–5 parts by weight of an unsaturated monocarboxylic acid taken from the group consisting of acrylic acid, methacrylic acid, cinnamic acid, atropic acid and crotonic acid and, correspondingly, about 60–25 parts by weight of a monovinylidene aromatic hydrocarbon, the particles of said

interpolymer having an average diameter of up to 0.5 micron.

5. The method of claim 4 wherein said polymer comprises (1) about 35–45 parts of 2-ethylhexyl acrylate, (2) about 3–10 parts of acrylonitrile, (3) about 2–5 parts of methacrylic acid, and, correspondingly, (4) about 60–40 parts of styrene.

6. The method of claim 4 wherein said polymer comprises (1) about 35–45 parts of decyl acrylate, (2) about 3–10 parts of acrylonitrile, (3) about 2–5 parts of methacrylic acid, and, correspondingly, (4) about 60–40 parts of styrene.

7. The method of claim 4 wherein said polymer comprises (1) about 35–45 parts of tridecyl acrylate, (2) about 3–10 parts of acrylonitrile, (3) about 2–5 parts of methacrylic acid, and, correspondingly, (4) about 60–40 parts of styrene.

8. The method of claim 3 wherein said polymer is a polymer of 40–90 parts of vinyl acetate and about 10 to 60 parts of an acrylate selected from the group consisting of n-butyl acrylate and 2-ethylhexyl acrylate.

9. The method of claim 8 wherein said polymer comprises vinyl acetate and n-butyl acrylate.

10. The method of claim 8 wherein said polymer comprises vinyl acetate and 2-ethylhexyl acrylate.

11. The method of claim 3 wherein said polymer is a polymer of 10 to 30 parts of butadiene and 70 to 90 parts of styrene.

12. The method of claim 3 wherein said resin is cyclized rubber.

13. The method of claim 3 wherein said resin is limed rosin.

14. The method of claim 3 wherein said resin is a pentaerythritol ester of rosin.

15. The method of claim 14 wherein said ester is the pentaerythritol ester of dimerized rosin.

16. The method of claim 14 wherein said ester is the pentaerythritol ester of maleated rosin.

17. The method of claim 3 wherein said resin is a copolymer of alpha-methyl styrene and vinyl toluene.

18. The method of claim 3 wherein said resin is a polyterpene resin.

19. The method of claim 18 wherein said polyterpene resin is terpene homopolymer.

20. The method of claim 18 wherein said polyterpene resin is the reaction product of terpene homopolymer and the condensation product of phenol and formaldehyde.

21. The method of claim 3 wherein said wax-like material is polyethylene having a maximum molecular weight of about 40,000.

22. The method of claim 3 wherein the particles further containing a long chain fatty amide.

23. The method of claim 3 wherein the particles further containing stearic acid.

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