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(54) Recording method

(57) An electrostatographic printing method is provided which comprises the steps of:-

1) Providing a toner bearing image on a receiving material which comprises on a suitable substrate at least one image receiving layer which comprises a particulate thermoplastic polymer which is characterised by an average particle size between about 1 μm and about 50 μm and at least one binder;

2) Fusing the toner bearing image and the coating to fix the toner image on the coated substrate.

The images produced by the method of the invention have good colour saturation and density together with the uniform surface gloss.

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Description

Field of the Invention

[0001] This invention relates to a method of producing images by electrostatographic recording processes, and in particular to a method for producing photographic-like output.

Background to the Invention

[0002] Electrostatographic printing is defined herein to include any printing or imaging technique wherein an image or print is produced by causing an ink or toner to transfer under the influence of an electric or electrostatic field. Various electrostatographic printing technologies such as xerographic, electrophoretic, electrographic, and electrophotographic printing are well known. Such systems are in wide commercial use, and allow for very high quality output of both images and text. This invention will be described in particular respect of office photocopiers and the like, though it is to be understood that it is applicable to other uses involving electrostatographic printing including for instance a laser electrostatographic printer or a digital colour electrostatographic printer such as the apparatus disclosed in United States Patent 5,499,093. The invention is also of use with electrostatographic printing techniques wherein an electrostatic field causes an ink or toner to be ejected from a nozzle and transferred to a suitable image receiving member, for instance the ink jet printing method disclosed in United States Patent 5,969,732 or the methods according to United States Patents 5,557,376 or 5,619,234.

[0003] According to one method of the electrostatographic technique a desired image is produced in the form of a charged pattern representing the image on an organic photoconductive dielectric recording member. Typically this member is in the form of a photoconductor coated drum and the image is produced when an overall electrostatically charged drum is imagewise exposed to conductivity increasing radiation such as visible light thereby destroying or dissipating the electrostatic charge in such exposed areas and producing a charge pattern on the drum. Toner is then electrically attracted to the charge on the drum and adheres to the drum. Lastly, the toner is transferred to an image-receiving substrate (typically paper) and bonded or fused onto the substrate by the application of heat and optionally pressure, resulting in permanent image formation on the substrate. Commercial electrostatographic printers normally incorporate a fusing station for fusing the toner to the surface of the material.

[0004] The electrostatographic recording process is capable of producing high resolution images on a wide variety of substrates. Because the image is formed by a pigment the image is stable, and because the image is thermally bonded to the paper the images are permanent and resistant to wear.

[0005] One limitation of this method, however, is the unavailability of a glossy print that resembles the prints available from the conventional photographic process. The glossy finish of such prints is well-known to enhance the intensity and attractiveness of the colour image. Because the toner image from electrostatographic recording lies on the surface of the substrate and is made of fine particles which scatter light there is a variation in gloss corresponding to different densities of colorant at different locations in the image area and it has been difficult to obtain a uniform glossy finish on the printed product. Thus the finished prints lack the appearance commonly associated with images produced by photographic processes and the perception that one is looking at photograph is not obtained. Even if a conventional glossy finish substrate such as transparent overhead material is used for printing, a uniform glossy image is surprisingly not obtained; the characters or image comprising the fused toner can still be made out from the rest of the otherwise glossy finish when one looks at the substrate off-angle.

[0006] Several methods and materials have been devised to produce glossy photographic-like output in non-photographic (i.e., non-silver halide) imaging processes such as the electrostatographic printing process.

[0007] For instance, one method of providing glossy final images from electrostatographic prnters is to laminate or encapsulate them. By lamination is meant the combination of a printed image with a transparent overlay, this combination usually being accomplished with an adhesive activated by heat, pressure, or both. By encapsulation is meant the combination of a printed image layer between two laminating sheets, that on the image surface being transparent, the combination being accomplished with an adhesive activated by heat, pressure, or both. A highly glossy image may be provided by lamination or encapsulation with a smooth glossy overlay which also acts as a physical protection for the image. However lamination and encapsulation are both expensive because additional materials are required together with additional handling and equipment, and there is considerable interest in finding a cheaper and simpler method providing glossy images from electrostatographic printers.

[0008] For instance Japanese Patent Application 4/333686 A reveals how the surface gloss of four colour (black, magenta, cyan and yellow) electrostatographic images may be controlled by changing the order in which the toners are laid down in a process that requires a two stage fuser process. The black toner has a higher softening temperature than the colour toners. For a glossy colour image the black toner is applied first and this is only partly fused during the first pass through the fuser process. Lower softening temperature colour toners (M, C and Y) are then laid down upon the black and when the image is again subjected to the fuser process these are completely melted to make a smooth surface

with high glossiness. For a less glossy image the colour toners are applied first and are again fully fused during the first pass through the fuser unit. The black toner is then applied on top of the 3 colour image, but because of its higher softening temperature this does not fully fuse during the second pass through the fuser unit leaving a dull or matt surface. The disadvantage of this process is that two passes through the fuser unit are required.

[0009] United States Patent 5,970,301 discloses a method whereby un-fixed toner images can be fixed to the substrate and provided with a desirable level of gloss in one single device, while widening the range of operating conditions without risk of offset occurring.

[0010] Furthermore United States Patent 6,060,203 discloses a material and method for producing photographic like output from an electrostatographic printing process through the use of specially coated substrates having a coating chemically "matched" to the image forming agent (i.e., inks, toners, etc.) used to form the image. The image is formed on the substrate and adheres thereto, and the combination is then fused to produce a uniform finish, preferably a glossy one. The chemical matching between the toner resin and the coating can be attributed to a number of factors, including the presence of like chemical groups, hydrogen bonding, or van der Waals attraction between the toner resin and the coating.

[0011] Additionally, due in part to the 'self levelling' nature of the coating under electrostatographic printing conditions, a uniform gloss coating is obtained after fusing.

[0012] However there is still a requirement for a general method of producing images from electrostatographic processes which compete with conventional photographic output.

[0013] The object of this invention is to provide a process for producing monochrome or colour images from electrostatographic printers that have good colour saturation and density together with the uniform surface gloss and overall impact that is associated with photographic prints.

Summary of the Invention

[0014] According to the present invention there is provided an electrostatographic printing method which comprises the steps of:-

1) Providing a toner bearing image on a receiving material which comprises on a suitable substrate at least one image receiving layer which comprises a particulate thermoplastic polymer which is characterised by an average particle size between about 1 μm and about 50 μm and at least one binder;

2) Fusing the toner bearing image and the coating to fix the toner image on the coated substrate.

Detailed Description of the Invention

[0015] The ink or toner may be a dry toner or a liquid toner, and typically comprises a colorant such as finely dispersed carbon black or an organic pigment and a thermoplastic binder consisting of a thermoplastic resin or a mixture of resins. A liquid toner additionally comprises at least one suitable solvent or carrier such as mineral oil, hydrocarbon, or other non-polar fluid. The toner may also contain other additives such as, for example, a dispersant for the pigment and a charge control agent. Suitable resins for use include transparent thermoplastic resins such as epoxy resins; polyesters; polyolefins such as polyethylene; polystyrenes and copolymers thereof such as styrene-(meth)acrylic resin and styrene-butadiene resin; (meth)acrylates; polyvinyl chlorides, polyvinyl acetates, and copolymers thereof such as copoly(vinyl chloride-vinyl acetate), or copoly (vinyl chloride-vinyl acetate-maleic acid); vinyl butyryl resins; polyvinyl alcohols; polyurethanes; and polyamides. During the fusing stage, the thermoplastic resin softens or partially melts sufficiently to 'fuse' the image to the substrate.

[0016] Suitable substrates to carry the layers of the invention include any of those commonly used for printing and imaging media, for example paper, high wet-strength paper, bond paper, tracing paper, treated paper such as resin or polyethylene coated paper, transparency materials, synthetic papers, and polymeric substrates such as cellulose acetates, poly(ethylene), poly (propylene), poly (vinyl chloride), and polyesters including poly (ethylene terephthalate) and poly (ethylene naphthalate). Preferably the substrate is paper based such as paper, resin coated paper, or polyethylene coated paper.

[0017] The particulate thermoplastic polymer for the image receiving layer is preferably additionally characterised by a Vicat softening point of between 50° and 170°C according to ASTM method D1525 and most preferably a Vicat softening point of between 70° and 120°C. Suitable thermoplastic polymers include low density polyethylene, copolymers of ethylene with other ethylenically unsaturated monomers, polypropylene, polyacrylates, acrylate copolymers such as styrene acrylate copolymers, polyamides, and polyurethanes. A preferable particle size for the particulate polymer is between about 5 μm and about 20 μm. A particularly suitable particulate polymer comprises low density polyethylene spherical beads having an average diameter of about 12 μm. Another particularly suitable particulate polymer comprises spherical beads of a 7% acrylic acid/ polyethylene copolymer having an average diameter of about 10 μm. Another suitable particulate polymer comprises polyethylene beads of random shape and an average particle size of about 12 μm to about 13 μm. These polymers have Vicat softening points of 70-100°C.

[0018] Preferably the binder is a hydrophilic binder.

Suitable hydrophilic binders include poly (vinyl alcohol) and copolymers of poly (vinyl alcohol); carbohydrates such as tragacanth gum, casein, or starch, and modified carbohydrates such as modified starch, hydroxyethyl cellulose or carboxymethyl cellulose; hydrophilic polyacrylates, methacrylates and acrylate copolymers; poly (vinyl pyrrolidone) and poly vinyl pyrrolidone copolymers; poly(ethylene imine); gelatin; and mixtures of such binders. A particularly suitable hydrophilic binder is poly (vinyl alcohol). A preferred hydrophilic binder is poly (vinyl alcohol) which has a degree of hydrolysis of at least 85%, and a particularly preferred binder is poly (vinyl alcohol) which has a degree of hydrolysis of between about 88% and about 98%.

[0019] A suitable dry coating weight for the image receiving layer is from about 5 to about 50 gm^{-2}. A preferred coating weight for the receiving layer is from about 5 to about 30 gm^{-2}, most preferably from about 15 to about 25 gm^{-2}. The ratio of the coating weight of the particulate polymer to that of the binder may be from about 20:1 to about 1:1, but preferably is between about 10:1 and about 5:1.

[0020] The receiving layer may optionally also comprise additives which are commonly added to image receiving layers such as surfactants to improve coating quality, cross linking agents, optical brightening agents, light stabilisers, biocides, and organic or inorganic pigments or fillers such as talc, chalk, silica, alumina, kaolin and the like.

[0021] One of the advantages of the present invention is that the coatings may be coated from aqueous formulations and that use of organic solvents is not required. The receiving layer may be applied to the substrate using any conventional coating method, such as air knife, doctor blade, or slide bead coating for example so as to obtain a good coating.

[0022] Optionally there may also be present additional layers in the assembly. Specifically there may be present between the substrate and the image receiving layer at least one fluid trapping layer. This aspect of the invention is especially preferred for use with liquid toners. In this aspect of the invention the fluid component of the liquid toner is held in the trapping layer and the colorant is held in the image receiving layer close to the surface to provide a bright image of good density and hue.

[0023] The fluid trapping layer may comprise one or more binders, optionally in combination with one or more absorbent fillers or pigments. Suitable binders for the fluid trapping layer include hydrophilic binders such as poly (vinyl alcohol) and copolymers of poly (vinyl alcohol); carbohydrates such as tragacanth gum or water-soluble starch derivatives; water-soluble cellulose derivatives such as hydroxyethyl cellulose, methyl hydroxypropyl cellulose, or carboxymethyl cellulose; water-soluble acrylate or methacrylate polymers and copolymers; poly (vinyl pyrrolidone) and vinyl pyrrolidone copolymers; gelatin, casein and mixtures of such binders. Alternatively the binder for the ink trapping layer may be a hydrophobic film forming resin polymer. Preferably the resin is a polymer of an ethylenically unsaturated monomer, i.e., a monomer having an ethylenically unsaturated bond. Examples of the ethylenically unsaturated monomer giving the polymer include acrylates having a C_1 -C_{18} alkyl group, such as methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, lauryl acrylate, 2-hydroxyethyl acrylate, and glycidyl acrylate; methacrylates having a C_1 -C_{18} alkyl group, such as methyl methacrylate, ethyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, and glycidyl methacrylate; and other ethylenically unsaturate monomers, such as styrene, a-methylstyrene, vinyltoluene, acrylonitrile, vinyl chloride, vinylidene chloride, vinyl acetate, vinyl propionate, acrylamide, N-methylolacrylamide, ethylene and butadiene. The polymer can be a copolymer of two or more ethylenically unsaturated monomers. Alternatively the resin polymer may be a polyurethane.

[0024] Suitable fillers for the ink trapping layer include clay, kaolin, talc, silica, calcium carbonate, diatomaceous earth, barium sulphate, titanium dioxide, aluminium oxide, zinc oxide, synthetic fillers, and mixtures of two or more of the above fillers. A preferred filler is synthetic amorphous silica or synthetic amorphous alumina.

[0025] The fluid trapping layer may optionally also comprise additives which are commonly added to image receiving layers such as for example surfactants to improve coating quality, cross linking agents, optical brightening agents, light stabilisers, and biocides.

[0026] The fusing stage may conveniently be performed using the fusing station which is normally incorporated in commercial electrostatographic printers.

[0027] Alternatively or additionally according to a second aspect of this invention the toner may be fused to the surface of the material using a subsequent heating step. This heating process may use any convenient method, such as heated air or infra red or microwave radiation. Alternatively the print may be heated under pressure by passing it through a nip between a pair of heated rollers. The material may be heated at temperatures above about 80°C so as to seal the surface; preferably to achieve a surface temperature between about 80°C and about 180°C, preferably between about 100°C and about 120°C.

[0028] According to another aspect of the invention, the printed image is heated under pressure with the image surface in contact with a second, inert sheet which is held against the image receiving layer of the material. The inert sheet does not adhere to the material, but protects it from the rollers used to apply the pressure. Further the inert sheet may be in the form of a sleeve around a roller or in the form of a loop passing round a series of rollers. Suitable inert sheets include polyester films, polyamide films, and casting papers. The inert sheet may be treated with silicones or ptfe to enhance the re-

lease properties. Furthermore a suitable choice of the inert sheet may be used to produce a desired appearance to the final image such as the use of a smooth inert sheet which will impart a high gloss to the image.

[0029] Preferably according to this aspect of this invention, the printed image is heated by passing through a laminator. By laminator is meant a device which is normally used for the lamination of printed images which comprises a means of heating and pressing together the image and the cover sheet, commonly by passing them through a nip between a pair of heated rollers. The rollers may have a suitable inert coating to prevent the image from adhering to them.

[0030] The toner bearing image may be provided by any electrostatographic imaging system such as a laser electrostatographic printer, a digital colour electrostatographic printer, an electrostatic ink jet printer, or a photocopier. This invention is also of particular interest when the exposure derives from an image in digital electrical form, wherein electrical signals modulate a laser beam or the light output of light-emitting diodes to produce the image on the drum. The coated paper may initially have a matt finish that is converted to a gloss or semi-gloss finish upon fusing during the electrostatographic process.

[0031] The following Examples will serve to illustrate the invention:-

Example 1

[0032] A formulation was prepared using the following components:-

Poly (vinyl alcohol) 10% solution	400g
Silicone surfactant	2g
Polyethylene beads	250g
Deionised water	348g

[0033] The poly (vinyl alcohol) used was a commercial sample from Harco under the trade name Mowiol 28-99 having a degree of hydrolysis of 99%. The surfactant was from BYK Chemie under the trade name BYK 348. The polyethylene beads were low density polyethylene spherical beads having an average diameter of about 12 μm available under the trade name Flowthene from Sumitomo. The formulation was coated on to a substrate comprising plain paper having a substance of 80gm^{-2} to give a wet coating weight of 100gm^{-2}, approximately 29·2 gm^{-2} when dry. A page was printed using an HP Laserjet 4 plus printer and fused with the fuser station of the printer to give a smooth clear dense print.

Example 2

[0034] A formulation was prepared using the following components:-

Poly (vinyl alcohol) 10% solution	400g
Silicone surfactant	2g
Polyethylene particles	250g
Deionised water	348g

[0035] The poly (vinyl alcohol) used was a commercial sample from Harco under the trade name Mowiol 56-98 having a degree of hydrolysis of 98%. The surfactant was as in example 1. The polyethylene particles were low density polyethylene particles of random shape and average particle size between about 12 and about 13 μm available under the trade name Coathylene HX1681 from duPont. The formulation was coated on to a substrate comprising plain paper having a substance of 80gm^{-2} to give a wet coating weight of 100gm^{-2}, approximately 29·2 gm^{-2} when dry. A page was printed using as in Example 1 to give a smooth clear dense print.

Claims

1. An electrostatographic printing method which comprises the steps of:-

1) Providing a toner bearing image on a receiving material which comprises on a suitable substrate at least one image receiving layer which comprises a particulate thermoplastic polymer which is **characterised by** an average particle size between about 1 μm and about 50 μm and at least one binder;
2) Fusing the toner bearing image and the coating to fix the toner image on the coated substrate.

2. A method according to claim 1 wherein the substrate is selected from paper, resin coated paper, polyethylene coated paper, high wet-strength paper, bond paper, tracing paper, treated paper, transparency materials, synthetic papers, cellulose acetates, poly(ethylene), poly(propylene), poly (vinyl chloride), and polyesters.

3. A method according to claims 1 or 2 wherein the particulate thermoplastic polymer for the image receiving layer is **characterised by** a Vicat softening point of between 50° and 170°C.

3. A method according to any of claims 1 - 3 wherein the particulate thermoplastic polymer is selected from low density polyethylene, copolymers of ethylene with other ethylenically unsaturated monomers, polypropylene, polyacrylates, styrene acrylate copolymers, polyamides, and polyurethanes.

4. A method according to claim 4 wherein the particulate thermoplastic polymer comprises low density polyethylene having an average particle size between 5 μm and 20 μm.

5. A method according to any of claims 1 - 5 wherein the binder for the image receiving layer comprises poly (vinyl alcohol) which has a degree of hydrolysis of at least 85%.

6. A method according to any of claims 1 - 5 wherein the dry coating weight of the image receiving layer is from 5 to 30 gm^{-2}.

7. A method according to any of claims 1 - 6 wherein there is present between the substrate and the image receiving layer at least one fluid trapping layer.

8. A method according to any of claims 1 - 11 wherein the toner bearing image is fused by heating under pressure by passing it through a nip between a pair of heated rollers.

9. A method according to claim 12 wherein the toner bearing image is heated to a temperature between 80°C and 180°C.

10. A method according to either claim 12 or 13 wherein the toner bearing image is heated under pressure with the image surface in contact with a second, inert sheet which is held against the image receiving layer of the material.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 01 2067

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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TECHNICAL FIELDS SEARCHED (Int.Cl.7)
G03G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 September 2002	Vanhecke, H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 02 01 2067

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