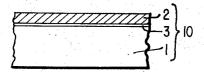
PROCESS FOR FIXING ELECTROPHOTOGRAPHIC IMAGES Filed Dec. 29, 1971

FIG. I



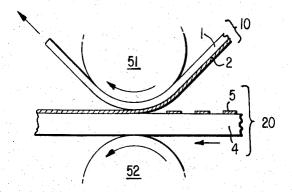


FIG. 2

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3,813,267 PROCESS FOR FIXING ELECTROPHOTOGRAPHIC IMAGES

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16 Claims 10

ABSTRACT OF THE DISCLOSURE

Electrophotographic images are fixed by applying thereto a fixing sheet comprising a supporting base and a clear adhesive resin layer, whereafter the adhesive resin layer is separated from the supporting base by heat and/or pressure and is thus allowed to transfer to surface bearing the toner image.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The invention relates to fixing processes for electrophotographic images.

(2) Description of the prior art

Conventional fixing processes for toner-developed images include fixing the image onto the base by dissolving the resin and other heat-soluble components contained in the toner under heat or with a solvent. If the image has been obtained by liquid development and is insufficient in its inherent capability to be fixed, it is usually coated with lacquer of covered with laminated clear film.

In addition to the difficulty in incorporating a lacquer coating system into compact equipment, coating with lacquer has been dangerous in that lacquer is volatile and ignitable in most cases, and harmful solvent vapors are easily generated.

As for coverage with a laminated clear film, although it offers a favorable solution to the two problems mentioned above, it provides a thick print, with the possibility of accompanying wrinkles, which has been a serious problem when the base (the material holding the image) is 45 thin.

SUMMARY OF THE INVENTION

The present invention relates to a process whereby the image can be fixed without the problems discussed above; characterized by the use of a fixing film or fixing sheet having freely separable clear thermoplastic resin layer.

The process of the present invention is such that the fixing sheet prepared by providing a clear thermoplastic resin layer on a supporting base is fixed onto the base bearing the electrophotographic toner image such that the toner image and the resin layer contact with each other, and the resin layer is pressed to adhere to the toner image bearing surface so strongly that it will be separated from the supporting base thereof under proper conditions (under heat and/or pressure or under the application of a solvent to the resin layer), whereby the resin layer is separated from its supporting base leaving the resin layer permanently fixed to the base.

A primary object of this invention is to provide a 65 new, improved method of fixing a toner image.

Another object is to provide an improved method of producing an electrophotographic print having an improved appearance and durability.

Further object is to provide a new improved method 70 for fixing toner images which requires less time and a more compact device than conventional methods.

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A still further object is to provide a toner image fixing method wherein a surface protective coating is laminated on the image with an improved degree of uniformity and a very small coating weight.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a sectional view of one fixing sheet used in the present invention.

FIG. 2 is a schematic view of one fixing sheet in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The process of the present invention will be explained in more detail by referring to the attached drawing in which FIG. 1 is a sectional view of the fixing sheet 10, which comprises a resin layer supporting base 1, a clear thermoplastic resin layer 2 and an intermediate layer 3 that controls the adhesiveness between the supporting base 1 and the resin layer 2. Intermediate layer 3, is, of course, not always necessary, depending upon the characteristics of the material.

The resin layer supporting base may be a plastic film, such as polyethylene terephthalate, diacetylcellulose, cellulose triacetate, polycarbonate, polypropylene, polyamide, polyethylene, regenerated cellulose, polystyrene or polyvinyl chloride, a wax-coated paper or mold release-coated. These may be surface-treated, e.g., moisture-proof cellophane. The plastic film is satisfactory even if it is opaque (pigment filled), or dyed.

Resin layer 2 is a clear resin layer which is held by the supporting base 1 under normal conditions, but which loses adhesion for the supporting base under pressure of generally 10-500 g./inch and preferably 10-300 g./ inch (where a silicone coated releasing paper was used as the support the pressure was about 20 g./inch or less, while polypropylene or polyethylene required 200-400 g./inch) and/or heat sufficient to soften the resin (for example, the adhesion between polystyrene and polyethylene terephthalate is broken at about 120° C. at which temperature the polystyrene is softened), or under the application of a solvent whereby when only the resin layer 2 is swollen with the solvent, the resin layer adheres to the toner bearing surface and the supporting base 1 is released, and is thereby transferred to uniformly cover the image. For this reason, it itself must be hard to decompose or degrade or discolor, and must be chemically stable. Furthermore, because of its role as the surface layer of the final print, the resin layer 2 cannot contain any chemical compound that renders it sticky or tacky at normal temperatures, and must have proper second order transition point (glass transition point).

Generally, a resin layer having a second order transition point of room temperature or above is preferred. Typical resin layers that meet these requirements include homopolymers and copolymers containing alkylacrylate, alkylmethacrylate, styrene, alkylstyrene acrylic acid, vinyl acetate, etc.

Adhesion between the resin layer 2 and the supporting base 1 may be controlled by the introduction of a small quantity of a functional monomer (a monomer containing functional groups which control the adhesive property of the copolymer such as acrylic acid, methacrylic acid, diethylaminoethyl methacrylate, hydroxylalkyl acrylate or methacrylate) up to 10% by weight of the whole polymer.

A multilayer structure may be employed for the resin layer, as is shown in FIG. 1. The resin layer must satisfy the following requirements. It must have a sufficient cohesive energy not to break along its thickness during a laminating operation. However, a very highly cohesive layer often adheres tightly to the surface of the sup-

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porting base and moreover will have a relatively high glass-transition temperature. Thus, if a multilayer structure is employed, the top coating 2 should have a low cohesive energy and high tackiness while the lower one 3 should be a hard, highly cohesive polymer of low tackiness. The layer 3 may also act to control (reduce) the adhesive energy with the supporting base 1. Thus, such multilayer structure enables a relatively low temperature and a hard, stiff, low-tacky, protective surface coating on the final print.

A multilayer resin layer may have a transition point lower than room temperature, provided that the surface thereof has a second order transition point greater than room temperature, e.g., about 25° C. up to about 100° C.

While the thickness of layer 2 is satisfactory if it ranges 15 from five to thirty microns, it is preferably 10 to 30

Layer 3 is an intermediate layer designed to control the adhesiveness between 1 and 2, and is satisfactory if it is very thin, usually it is 0.1 to 6 microns. Where only layer 20 2 is present it may have a tendency of break in certain instances; however, when layer 3 is present the whole layer is transferred. Layer 3 can contact with layer 2. It may be colored when it adheres to layer 1. It must be clear where layer 2 is transferred onto the base bearing the image accompanied by intermediate layer 3, where the latter has a higher second order transition point than the former and both layers do not melt and flow into each other. In such a case, layer 2 is composed of a comparatively soft resin (that is, a resin having low cohesive energy and a low second order transition point and which is tacky—especially becoming tacky at a temperature of a few degrees above room temperature), and thus when it is passed against the toner image it is easily deformed 35 and acts to fill in the voids between toner particles. Meanwhile, layer 3 suppresses the blocking property of such a soft resin layer.

FIG. 2 illustrates the fixing sheet as shown in FIG. 1 facing and being pressed in to contact with element 20 40 bearing the toner image 5 on the base 4.

Element 20 may be either a developed electrofacsimile paper or a copying sheet bearing the toner image transferred thereto from a selenium drum or the like. It may also be an organic photoconductive film.

Two pieces of sheet-like material can be equally pressed together while held between pinch rolls 51 and 52 in such a manner that no wrinkles are developed. Rolls 51 and 52 may, of course, be heated pressure rolls.

The toner image bearing surface of element 20 may 50 be coated with a small quantity of a solvent (to solvate the resin layer 2 of the fixing sheet 10). A particularly preferred embodiment is provided when the sheet 20 is a photoconductive sheet that permits toner image 5 to be developed by a liquid development, the surface thereof 55 containing a small quantity of an insulative liquid uniformly spread thereon.

The insulative liquid may be either the carrier of the liquid developer or a rinse liquid used to clear the sheet of residual developer left after the development. In such a 60 case, a combination such as will loosen the resin layer is selected. Since developing and/or rinse, the liquids usually have a low solubility parameter and are often nonpolar liquids, such as isoparaffins, n-paraffins, hydrocarbon chlorofluoride, long chain alkylacrylates or polymers 65 containing long chain alkylmethacrylates or styrene are the most preferred resins used. Thus, since a carrier liquid of liquid developer such as n-paraffine or iso-paraffine may suitably be used as the solvent, a resin which is soluble in or swellable to the liquid and which has an appro- 70 priate second order transition point is preferred. In fact, the amount of the liquid remaining on the toner bearing surface will be very small, usually about 10-25 g./m.2, which is comparable to the coating amount of the resin, and thus the resin layer does not flow out. Also resins 75 sticky. 4

which are adhesive to the toner bearing surface are preferred.

In FIG. 2, either roll 51 or roll 52, or both, are preferably heated. When the film is heated to 100° C. or so, the difference in the degree of resulting thermal expansion between the base 1 and the adhesion layer 2 gives rise to a force in between the layers 2 and 3, or between layers 3 and 1, causing them to separate from each other, the amount of thermal expansion of layer 3 being relatively large preferably.

Alternatively, when a liquid is diffused from the photosensitive layer side to the adhesion layer 2 to loosen the latter, the adhesion between the layers 2 and 3, or between the layers 3 and 1, is reduced causing the separation. Thus, only layer 2 or layers 2 and 3 are left on the photosensitive layer, as shown in FIG. 2. The supporting base may be reused repeatedly or abandoned after one

The advantages of the present invention are enumerated hereinafter:

- (a) A print having a glossy surface without looking as if a thick film was spread over the image can be obtained.
- (b) A supporting base lower in cost than a film can be when it adheres to layer 2. One desirable embodiment is 25 utilized, such as paper or film easy to discolor or decompose. The foregoing film would be laminated.
 - (c) The effect of improving the image density as is given by coating with lacquer (due to scattered light of the toner image) can be obtained.
 - (d) The necessary apparatus is easily incorporated into existing equipment.
 - (e) In case the film is laminated, it may often be intensely curled, whereas the method of the present invention reduces such a possibility to a considerable extent. The reason for this reduction in the possibility of curling may be the reduction in thickness. That is, a conventional laminate film comprises 10-20 microns of adhesive layer and at least 25 microns (which is the thinnest film known to be available) while in the instant invention, a laminated film of 5-30 microns is sufficient. Another reason may be that the film support used in a conventional laminate film comprises a polymer which has relatively high mechanical strength, while according to our invention the resin layer may have a relatively low molecular weight, thus low internal cohesive energy.

The process of the present invention will now be explained in more detail by referring to the following examples.

EXAMPLE 1

One side of a polyethylene terephthalate film (80 microns in thickness) was coated with a xylene solution of polystyrene (degree of polymerization-about 2500 and 2% by weight in concentration) in such a manner that the dry coverage would be 1.0 g./m.2.

The film was then overcoated with a 10% by weight solution of methanol-ethyl acetate mixed with polyvinyl acetate (1:1 by weight, the polymerization degree of the polyvinyl acetate being about 200) in such a manner that the dry coverage would be 10 microns.

The fixing film thus obtained was combined with a photoconductive sensitive layer composed of a silicon resin (resin is methyl phenyl polysiloxane, the molecular weight of which is about 1000) and zinc oxide, which were coated on a paper base. The ratio of the zinc oxide to the silicone resin was 100 parts to 25 parts by weight, respectively. A toner image was formed on the photosensitive paper by development with a magnetic brush. This photosensitive paper and the fixing film were contacted together so that the photosensitive surface and the polyvinyl acetate adhesion layer thereof contacted each other, and were run through heated rolls as shown in FIG. 2. where the roll temperature was 120° C. When heated, the polyvinyl acetate film separated from the polystyrene layer, providing a glossy print. The print surface was not

A biaxially stretched polypropylene film (30 microns in thickness) was coated with polybutyl methacrylate (20 microns in thickness having a polymerization degree of about 170) without pretreatments such as corona-treat- 5 ment or the like.

The fixing film thus obtained was combined with a photosensitive paper having a zinc oxide photosensitive layer with styrenated alkyd resin (Styresol 4250 made by Japan Reichhold Chemical) as the binder, the ratio of 10the zinc oxide to the binder being the same as in Example 1. The toner image was formed using a liquid developer with an isoparaffin type solvent (Isoper H made by Esso Standard Oil Co.) as the carrier. While a thin layer of developer was still wetting the photosensitive 15 layer uniformly, the film was put thereupon and the toner image was transferred to the adhesion layer at an adhesion temperature of 70° C. in the same manner as in Example 1. A glossy print as obtained in Example 1 resulted.

This is a heat-solvent example. After the isoparaffinic solvent is volatilized, the adhesion is not well carried out. The isoparaffinic solvent presumably slightly swells the polybutylmethacrylate at 70° C., but the isoparaffin does not volatile completely. Thus, this operation should pref- 25 erably be done before complete drying which is in accord with one of the purposes of the invention—that is, to provide a print by a compact processor in short time.

EXAMPLE 3

A polyethylene terephthalate film (80 microns in thickness) was provided directly with a coating composed of a copolymer of styrene, ethylhexyl methacrylate and hydroxyl ethylacrylate (copolymerization ratio: 30, 60 and 10). The coating was done with a 10% solution of butyl acetate to a thickness of 20 microns. The toner image could be transferred to the photosensitive layers used in both the embodiment 1 and embodiment 2 under heat.

EXAMPLE 4

An organic photoconductive film was obtained by adding Methylene Blue (1 part by weight) and tetracyanoquinodimethane (1 part by weight) as sensitizers and diphenyl chloride (15 parts by weight) as a plasticizer to a 45 copolymer of n-vinyl carbazol and ethyl acrylate (100 parts by weight). This composition was coated onto a polyethylene terephthalate film with an evaporated film of cuprous iodide.

As the fixing film, a silicon mold release paper coated 50 with a copolymer of methyl methacrylate and ethyl acrylate (the ratio of the methyl methacrylate to the ethyl acrylate being 50/50 by weight) was utilized. The photoconductor film and fixing film were contacted between heated rolls as shown in FIG. 2 and heated to 120° C. 55 for transfer, resulting in a print as satisfactory as the one obtained in Example 1. A force of 20 g./inch was necessary to peel the strip off the film.

The present invention generally speaking includes two basic embodiments: namely, embodiment A which is di- 60 is polyethylene terephthalate, the inner layer polystyrene rected to a process of forming a thermoplastic resin layer on a surface bearing a toner image which comprises bringing under heating the surface into contact with the thermoplastic resin layer applied on a (temporary) support, said thermoplastic resin layer being more adherent to said 65 surface bearing toner image than to said support under heating, and releasing the support from the thermoplastic resin layer to leave the thermoplastic resin layer on the surface; and embodiment B which is directed to a brought into contact with the thermoplastic resin layer in the presence of a solvent or a swelling agent for the thermoplastic resin and that the thermoplastic resin layer is more adherent to the surface in the presence of the solvent or the swelling agent.

In a process of embodiment A, the second order transition point of the thermoplastic resin is typically lower than that of the support and heating occurs at a temperature near the range of the second order transition point of the thermoplastic resin.

In a process of embodiment B, the solubility (or swelling amount) of the resin to the solvent may be larger than that of the support or the support is substantially insoluble in the solvent or is substantially not swellable by the swelling agent.

In embodiment A, the support may have a second order transition point about 40° C. and not show adherent and flowing properties below 150° C. Examples are polyethylene terephthalate, nylon, etc.

In embodiment B, the support may not be soluble or not strongly swellable to a non-polar solvent such as straight chain or branched chain hydrocarbons. In this case, the support has relatively low transition point, an illustrative material being polyethylene.

In embodiment A, the resin may have a low transition point relative to the base (usually, below room temperature) and it becomes strongly adherent when heated at about 100° C.

In most cases, the resins for embodiments A and B are identical.

Numerous modifications of the invention will become apparent to one of ordinary skill in the art upon reading the foregoing disclosure. During such a reading it will be evident that this invention provides a unique process for fixing electrophotographic images for accomplishing the objects and advantages herein stated.

What is claimed is:

- 1. A process for fixing electrophotographic image characterized by fixing a toner image in such a manner that a fixing sheet composed of a supporting base and a clear adhesion resin layer is placed upon the material bearing the toner image so that the adhesion layer and the surface bearing the toner image may contact each other and the adhesion layer is separated from the supporting base under heat and/or pressure and/or solvating action and thus is transferred to uniformly cover the surface bearing the toner image, the clear adhesion layer being retained thereon to thereby fix the toner image to said material.
- 2. A process as in claim 1 where said material bearing the toner image was 5-25 g./m.2 of volatile carrier liquid of liquid developer applied thereon.
- 3. A process as in claim 2 where said volatile liquid is an isoparaffinic solvent and said resin layer comprises a polymer of a long-alkyl (having 4 or more carbon atoms) ester of methacrylate.
- 4. A process as in claim 1 where said layer to be released comprises two layers, the inner layer (which becomes part of the surface layer in the final print) having a higher second order transition point than that of the outer layer.
- 5. A process as in claim 1 including an inner layer present between said supporting base and said resin layer.
- 6. A process as in claim 5 where said supporting base and the resin layer a resin which is incompatible with the polystyrene and has a lower second order transition point than that of the polystyrene.
- 7. A process as in claim 1 where the thickness of the resin layer is 5 to 30 microns.
- 8. A process as in claim 1 of forming a thermoplastic resin layer on a surface bearing a toner image which comprises bringing said surface in contact with a thermoprocess of embodiment A expecting that the surface is 70 plastic resin layer applied on a support, said thermoplastic resin layer being more adherent to said surface bearing the toner image than to said support under heating, and heating said toner bearing surface, said support and said resin layer while the toner bearing surface and the resin 75 layer are in contact and releasing said support from said

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thermoplastic resin layer to leave said thermoplastic resin layer on said surface.

- 9. A process as in claim 8 where the second order transition point of the thermoplastic resin is lower than that of the support and heating at a temperature near the range of the second order transition point of the thermoplastic resin.
- 10. A process as in claim 8 where the support has a second order transition point above 40° C. and does not show adherent and flowing properties below 150° C.
- 11. A process as in claim 8 where the resin has a low transition point relative to the base and becomes strongly adherent when heated at about 100° C.
- 12. A process as in claim 11 where said transition point is below room temperature.
- 13. A process as in claim 1 of forming a thermoplastic resin layer on a surface bearing a toner image which comprises bringing said surface in contact with a thermoplastic resin layer applied on a support, said thermoplastic resin layer being more adherent to said surface bearing toner image than to said support in the presence of a predetermined solvent or swelling agent, and contacting said toner bearing surface, said solvent and said resin layer with said solvent or swelling agent while the toner bearing surface and resin layer are in contact thereby

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releasing said support from said thermoplastic resin layer to leave said thermoplastic resin layer on said surface.

- 14. A process as in claim 13 where the solubility or the swelling amount of the resin to the solvent is larger than that of the support.
- 15. A process as in claim 13 where the support is substantially insoluble in the solvent or substantially not swellable in the swelling agent.
- 16. A process as in claim 13 where the support is not soluble or not strongly swellable in a non-polar solvent selected from the group consisting of straight chain and branched chain hydrocarbons.

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