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OSAMU FUKUSHIMA ET AL

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MOLTEN IMAGE TRANSFER IN ELECTROPHOTOGRAPHY

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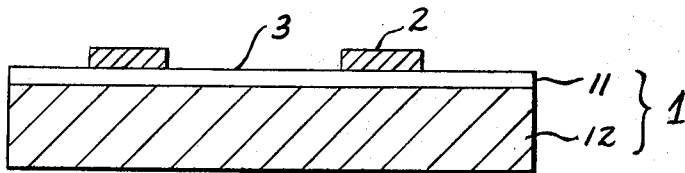


FIGURE 1

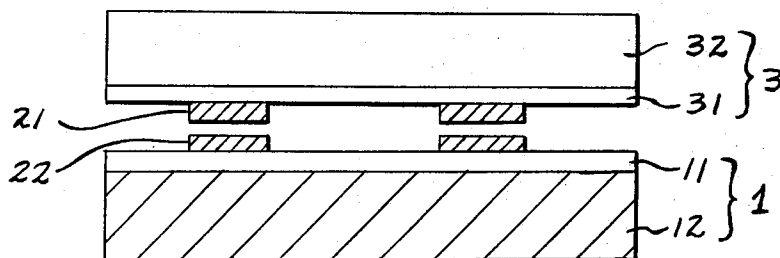


FIGURE 2

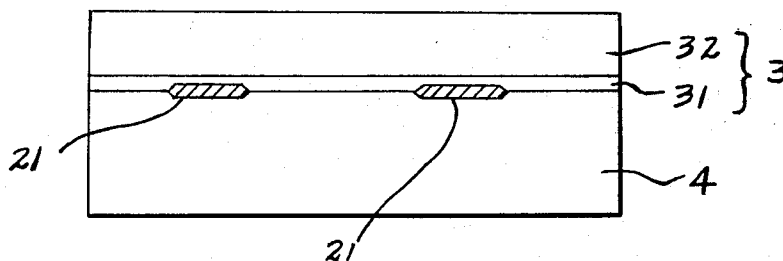


FIGURE 3

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MOLTEN IMAGE TRANSFER IN ELECTROPHOTOGRAPHY

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7 Claims

ABSTRACT OF THE DISCLOSURE

A process of transferring a toner image obtained by electrophoretic development comprising employing a liquid developer containing a thermoplastic resinous material which is included in the developed image, forming an image on an electrophotographic recording layer, bringing a heat-sensitive adhesive tape into an intimate contact with said image, heating the assembly so as to soften the resinous material included in the developed image but not to soften the heat-sensitive adhesive layer whereby the image is perfectly transferred to the adhesive tape, separating the tape from the recording layer and finally laminating the image-bearing tape onto a suitable support by softening the adhesive layer.

It should be noted that the recording layer does not melt nor soften at the temperature at which the developed image is softened and transferred.

This invention relates to a transfer and fixing method of an electrophotographic toner image with the use of a heat-sensitive adhesive tape without any loss or lowering of image quality.

Conventionally, an electrophotographic toner image has been transferred electrostatically or by pressure. A toner image obtained by electrophoretic development would not perfectly be transferred onto another surface because of the extremely fine particle size of the toner which is prone to be firmly trapped in the minute irregularities present in the developed surface. Heretofore, transfer of such image was mechanically carried out by contacting with the developed surface a porous sheet which readily adsorbs the carrier liquid of the developer while it is still wet with the developer. Alternatively, partial or fractional transfer of an electrophoretically developed image has been accomplished by uniformly applying a solvent which can dissolve the resinous component included in the developed image but not the photoconductive layer and then super-imposing a porous transfer sheet on the layer whereby the image becomes sticky and adheres to the transfer sheet. Though these methods are now in practical use in the preparation of a contact-printing master for diazo print in the office copying field, a perfect toner transfer is hardly expected to occur. Therefore, they are only applicable for half-toner or lee images. A more advanced technique is requested for a perfect transfer of a continuous tone image without any loss of image quality.

Accordingly, the principal object of the present invention is to provide an improved toner transfer method which meets this requirement. The present invention provides a new transfer and fixing method of a toner image formed by electrophoretic development of an electrostatic latent image on a photoconductive insulating layer through any one of the techniques known in the art of electrophotography. The method comprises pressing a heat-sensitive adhesive tape on a photoconductive layer bearing a developed toner image so as to form a firm bond between the toner image and the adhesive, then peeling off the adhesive tape from the layer and laminating the toner image bearing adhesive tape onto a final substrate to

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form the end product (print). The method is characterized by the following features:

(i) The toner image formed by electrophoretic development contains a thermoplastic resinous material.

(ii) Said resinous material in the toner image has a lower softening point than both of the heat-sensitive adhesive coating of the tape and of the photoconductive layer.

(iii) The adhesive transfer of the toner image is carried out at a temperature higher than the softening point of the toner image (said resinous material) but lower than those of the adhesive and the photoconductive layer.

(iv) The lamination of the adhesive tape on the final substrate is carried out at a temperature where the adhesive of the tape melts to such a degree as to form a firm bond with the substrate surface.

The practical operation of the present method is quite simple though it may seem complex from the above descriptions, making it possible to carry out toner transfer without any loss of image quality to obtain an image on any type of substrate at one's option with a glossy fine appearance substantially equivalent to that of the conventional silver halide photographic print. It should be noted that in the present method the amount of toner not transferred to the adhesive tape but remaining on the photoconductive layer is usually negligibly small.

The present invention will be explained more in detail referring to the accompanying drawings.

FIG. 1 illustrates a cross-sectional view of a photoconductive recording material 1 carrying a toner image 2 obtained electrophoretically on the photoconductive insulating layer 11 which is provided on a backing 12. The toner image 2 comprises a colored pigment or dye and a thermoplastic resinous material. Suitable pigments include carbon black, phthalocyanine blue, brilliant carmine 6B, benzidine yellow, and phthalocyanine green, while alkali blue is one example for suitable dyestuff. Thermoplastic resinous materials contained in the toner image include vegetable oil modified alkyd resins (medium to long oil length), epoxyester resin, rosin modified phenol-formaldehyde resin, hydrogenated rosin ester with glycerol, pentaerythritol ester of rosin, xylene-formaldehyde resin, copolymers containing alkyl acrylate, polystyrene, copolymers including styrene, hydrocarbon resin, ethylcellulose, vegetable oils, vinyl chloride/vinyl acetate copolymer, polyamide resin, etc.

Many of these are known as thermosetting resin, but what is meant by "thermoplastic" here is that they exhibit thermoplasticity or they can be softened upon heating at the step of toner transfer.

Among these resins, those having softening points lower than 90° C. are generally preferred.

Thermoplastic properties stated in this invention mean, apart from strict technical definition, that exhibit a heat softening performance when the image transfer operation is carried out, although most of alkyd resins and epoxyester resins are classified as thermosetting materials.

Toner image transfer in accordance with the invention is not successfully carried out with a toner image which contains an alkyl or epoxyester resin and which has been left in air prior to the transfer operation, since the curing of the resin by oxygen has took place and the resin has lost its thermoplastic property.

Many of the commercially available developers contain antioxidants to prevent the curing of thermosetting resins included therein, whereby the curing after development is markedly retarded.

From the practical point of view, however, the above-cited apprehension is only an over-anxiety since the transfer operation is accomplished in a few hours after development.

Generally these resinous materials are employed to control the electrophoretic properties of the dispersing particles in liquid developers and to impart the developed image a self-fixing property and used in many cases jointly with nonionic or anionic surface active agents or other additives. In practicing the invention, the composite, i.e., resinous material and other additives, should exhibit a softening point lower than the above-cited value. By the way, part of resinous material which are soluble in the carrier liquid is thought firmly associated with the surface of the dispersed pigment as a result of a prolonged blending of the pigment with such resinous materials. Therefore, a developed toner image may in most cases include resinous materials.

In FIG. 1, 3 designates a toner-free or background area. Construction of the photoconductive layer will be given later.

FIG. 2 illustrates the cross-section of the assembly consisting of a heat sensitive adhesive tape 3 and the developed photoconductive recording member 1 shown in FIG. 1. The two sheet materials are held in an intimate, mutual contact under a suitable temperature condition where only the toner image is softened undergoing adhesive transfer from the photoconductive surface 11 to the adhesive coating 31 which is supported by a base 32. The heat-sensitive adhesive coating 31 has a softening temperature higher than the toner image. The two-ply assembly is fed with sufficient heat and pressure so as to cause softening and transfer of the toner image but not the softening of the coating 31 by means of a pair of heating rolls, electric iron or other devices whereby the substantial portion 21 of the toner image 2 is transferred onto the coating 31 leaving a residual image 22 on the photoconductive layer 11. Here of course, the photoconductive layer 11 should not soften or adhere to the adhesive coating. Since the photoconductive layer 11 must meet this single requirement, any of those having a relatively high softening point may be utilized for the present invention. Typical photoconductive layers comprise:

(i) Mixtures of an insulating resinous binder and a finely divided photoconductor selected from zinc oxide, titanium dioxide, cadmium sulfide, zinc sulfide, zinc cadmium sulfide, cadmium selenide, calcium strontium sulfide, mercury iodide, mercury oxide, mercury sulfide, indium trisulfide, gallium triselenide, arsenousdisulfide, arsenic trisulfide, antimony trisulfide, cadmium sulfoselenide, and mixtures of these:

(ii) Vacuum deposited coatings comprising selenium selenium-telluride, selenium-sulfur, selenium-arsenic, etc.;

(iii) Coatings comprising inorganic photoconductors such as zinc oxide, or zinc sulfide and glass binder; and

(iv) Coating containing organic photoconductors. Suitable organic photoconductive compounds include

triphenylamine,
2,4-bis(4,4'-diethyl-aminophenyl)-1,3,4-oxadiazol,
N-isopropylcarbazol,
triphenylpyrrol,
4,5-diphenylimidazolidinone,
4,5-diphenylimidazolidine-thione,
4,5-bis(4'-aminophenyl)-imidazolidinone,
1,5-dicyanonaphthalene,
1,4-dicyanonaphthalene,
aminophthalodinitrile,
nitrophthalodinitrile,
1,2,5,6-tetra-azacyclooctatetraene-(2,4,6,8),
2-mercapto-benzothiazole,
2-phenyl-4-diphenylideneoxazolone,
6-hydroxy-2,3-di(p-methoxyphenyl)-benzofuran,
4-dimethyl-aminobenzylidene-benzohydrozide,
3-benzylidene-amino-carbazol,
polyvinylcarbazol,
(2-nitro-benzylidene)-p-bromoaniline,
2,4-diphenylquinazoline,

1,2,4-triazine,
1,5-diphenyl-3-methylpyrazoline,
2-(4'-dimethyl-aminophenyl)-benzoxazol,
3-aminocarbazol phthalocyanine, and

5 mixture therebetween. Available for this invention are such organic photoconductive materials as disclosed in Japanese patent publication No. 8,553/66 (corresponding to U.S. Pat. No. 3,418,116), No. 19,751/67, No. 25,230/67, No. 2,629/68, No. 24,753/68 and No. 27,588/68.

When a photoconductive layer contains a thermoplastic resinous material as insulating binder (the first group) or as a photoconductor (the fourth group), a care must be taken to meet the requirement as regards the softening point of the layer, one of the most effective way of satisfying the condition is to crosslink or cure the resin so as to form a three-dimensional molecular network. Suitable thermosetting resins include alkyd resins, vinyl monomer (styrene, acryl esters) modified alkyd resins, epoxyester resin, polyurethane, unsaturated polyester, phenol-formaldehyde, thermosetting acrylic resins, melamine-formaldehyde, silicone-alkyd resins.

It is also preferable to use a photoconductive layer having a low-adhesive surface such as is provided with a silicone release coating which is disclosed in Japanese patent publication No. 28,037/69 or containing a fluoro-carbon resin as binder or surface release coating.

Most preferable formulations may be given by photoconductive layers comprising photoconductive zinc oxide or cadmium sulfide dispersed in a binder consisting alkyd epoxyester, or vinyl copolymers containing primary OH group and polyisocyanate as curing agent for the former. One prominent feature of such layers is a low-contrast tone reproduction property. Even in the case where the binder is thermoplastic, the photoconductive layer sometimes shows little tendency to stick to the adhesive coating due to the high concentration or the photoconductive particles incorporated, permitting the practice of the present invention.

On the other hand plasticized organic photoconductive layers are not suited for the invention because of the low melting point of many plasticizers. To avoid this difficulty one may employ a rigid support such as metal drum, metal plate in place of flexible one like paper and use an organic photoconductive layer free of plasticizers.

The tape bearing the final image may be laminated on a flexible support such as paper or plastic film such as polyethylene, polypropylene, polystyrene, polyvinylchloride, polyvinylidene chloride, regenerated cellulose, cellulose diacetate, cellulose triacetate, nitrocellulose, cellulose acetobutyrate, polycarbonate, polyethyleneterephthalate, etc.

Among these, polypropylene, cellulose acetate, cellulose acetobutyrate, and polyethyleneterephthalate are most preferred as regards clearness and resistance to discoloration, since the present process is adapted to provide electrophotographic prints of an excellent quality.

Besides, opaque bases such as metal foil, paper or fabrics may also be used.

The thickness of the base film for the adhesive tape may range from 5 to 200 microns, and more preferably 3 to 30 microns.

The heat sensitive or hot-melt adhesive coating 31 in the figure may be composed of any formulation known in the art with due consideration to the softening point, and the compositions of the toner and the photoconductive layer to be combined therewith.

The heat-sensitive or hot-melt adhesive coating may comprise low-molecular weight component selected from coumaronindene resin, rosin and its derivatives, mineral oil, wax, petroleum hydrocarbon resin, vegetable wax, terpene resin, alkyd resin, and thermoplastic phenol-formaldehyde resin.

The coating may also contain as the component to impart internal strength of the adhesive layer ethylcellulose,

polyvinylacetate, polybutylmethacrylate, polyethylene, ethylene vinyl acetate copolymer, polystyrene, styrene copolymers, and polyisobutylene; recently polyamide, polyamide derivatives, and polyvinylacetate are increasingly used. Formulation of the heat-sensitive adhesive is found, for example, in "Handbook of Adhesives" by Skeist published from Reinhold Publishing Co. (1962) from 447 to 451.

Ordinarily, the heat-sensitive coating begins to soften or melt near 80° C. showing a sufficient flow above 90° C. On the other hand, a toner image contains components such as vegetable oil or long-oil alkyd resin which melt or flow below 80° C. Therefore, the transfer of the toner image onto the adhesive coating may be successfully carried out at 70 to 90° C. under suitable pressure and heating time scale. This is, of course, a standard measure for settling the transfer operation conditions. In case where the adhesive coating provided on a high temperature resistant base (for example polyethylene-terephthalate) melts at a higher temperature, transfer may be practiced at a higher temperature. In summary, a temperature of transfer may be selected so as to meet the above-noted requirement.

FIG. 3 shows the adhesive tape carrying the toner image transferred thereon firmly bonded on a final support 4. At the fixing operation the coating 31 is heated to sufficiently melt and firmly adhere on the surface of the support 4. The support 4 may be of any material such as paper, opaque plastic film, metal plate, etc., according to various purposes. With an opaque support 4, the final print may be viewed by reflection. When a transparent support is used, a transparency for overhead projector lantern slide may be provided. The transparent support may be made of those materials suitable for base 32.

The present process may be utilized not only to obtain a monochromatic print but to produce a multicolor print by transferring a multicolor image formed by electrophotographic over-print technique.

EXAMPLE I

In this example, a commercially available heat-sensitive adhesive tape was used which comprised 12 micron thick polyethyleneterephthalate film coated on one surface with polyvinyl acetate as the primary component. This coating softened near 100° C.

An electrophotographic sheet material was prepared by forming a photoconductive electrophotographic layer on a 100 micron thick baryta paper which had been subbed with an electroconductive material. The photoconductive coating composed of 100 parts of zinc oxide, 14 parts of styrenated alkyd resin and 6 parts of polyisocyanate compound, the thickness of the coating being 10 microns on dry base. Since this layer was heated at 50° C. for a long time so as to cure the alkyd resin, the layer would not soften or become tacky near 100° C.

The light-sensitive sheet after completely dark-adapted was charged with a uniform electrostatic charge of negative polarity, exposed to an optical image and then treated with a liquid developer prepared by dispersing 1 part of a commercially available offset printing ink under the trade name "Plano Blue" from Fuji Photo Film Co., Ltd. into 400 parts of kerosene under the irradiation of ultrasonic wave.

A faithful reproduction of tonal gradation resulted with the use of a development electrode during development.

The treated sheet was rinsed with isoparaffinic solvent, substantially dried, and superimposed with the adhesive tape in such a manner that the adhesive coating faces with the toner image. The assembly was inserted between a pair of stainless rollers kept at 80° C. The passed sheets could be peeled off from each other quite easily without any tendency to block whereby only the toner image was transferred onto the adhesive coating. While the maximum density of the developed image before transfer was 2.0, the density of the same area dropped to 0.3 after

transfer. No photoconductive layer was transferred at the background area. The adhesive tape bearing the toner image was then laminated on the baryta coating of photographic baryta paper about 120 microns thick and the assembly was passed between a pair of rollers heated to 130° C. The final print thus prepared exhibited a maximum density of 1.8 (reflection density).

EXAMPLE II

On an aluminum pipe was formed an electrophotographic layer comprising 100 parts of cadmium sulfide and 30 parts of a thermosetting acrylic resin which was cured at 200° C. This member was subjected to corona charging after complete dark-adaptation and then to image exposure. A liquid developer prepared in the following manner was applied on the pipe.

Preparation of the developer

The following ingredients were thoroughly mixed by means of a high-speed mixer:

Microolith Blue 4G-T	mg--	200
A varnish obtained by cooking rosin modified phenol-formaldehyde resin with linseed oil	mg--	400
Toluol	ml--	10

Here rosin modified phenol resin is such as is used for printing inks and has a viscosity of about 100 cp. This resin is soluble in kerosene, but not in acetone, linseed oil, nor isoparaffinic hydrocarbon solvents. It completely dissolves in cyclohexane.

The resulting bluish concentrated paste was dispersed in a mixture comprising 250 ml. of kerosene, 700 ml. of cyclohexane and 50 ml. of linseed oil.

The developed member was repeatedly rinsed in Isopar E (an isoparaffinic solvent with KB value of 29 available from Esso Standard Oil Co.).

By the way Microolith is a pigment flushed with hydrogenated rosin ester marketed by Ciba Ltd. On the surface of the developed member was pressed a heat-sensitive adhesive tape comprising 20 micron thick polypropylene film coated with an adhesive substantially comprising an aliphatic polyester resin in such a manner that the adhesive coating faces the paper surface at 75° C. Since this adhesive coating is not activated until near 100° C. the tape could be easily removed from the surface only with the toner image transferred onto the adhesive coating. The toner image bearing tape was then laminated and firmly bonded with a 100 micron thick polyethyleneterephthalate film at 110° C. to form a transparency.

EXAMPLE III

In this example, a multi-colored image is formed with the use of zinc oxide coating and a set of color-separation positives.

First of all, a set of color-separation positive transparencies were prepared from a photographic color negative employing blue, green and red filters. Each of these shall be called yellow, magenta and cyan printing positive, respectively.

The zinc oxide electrophotographic material used was prepared by coating aluminized polyethyleneterephthalate film with a layer comprising 100 parts of zinc oxide, 20 parts of epoxyster of dehydrated castor oil fatty acid, and 0.2 part of cobalt naphthenate, and thermally curing said layer.

A sheet of the thus prepared film was negatively charged at darknes, exposed to the magenta printing positive, and developed with a magenta developer described below. The development was carried out with the use of a development electrode for 2 minutes. Then the sheet was subjected to a high-speed flow of Isopar E briefly, passed between a pair of squeeze rollers to squeeze the rinsing liquid, and then dried with a drier. These operations were carried out under subdued light. The same sheet was again charged negatively, exposed to the cyan printing positive and immersed in a cyan developer shown

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below. Further, similar operations were repeated. Finally exposure to the yellow printing positive and development with a yellow developer were carried out. Thus, a multi-colored print resulted by overprinting technique.

Preparation of the developers

Magenta.—A concentrated paste obtained by blending the following components was dispersed in a mixture comprising 200 ml. of kerosene, and 800 ml. of cyclohexane.

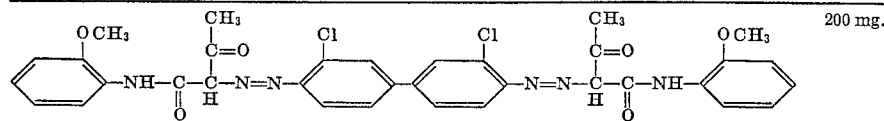
	Mg.
Brilliant Carmine 6B	200
Soybean oil modified long oil alkyd	400
Polymerized linseed oil	100

Cyan.—A concentrated paste obtained by blending the following ingredients was dispersed in the same mixture as for the magenta developer.

	Mg.
Phthlocyanine Blue	200
Medium oil length epoxyester of dehydrated castor oil fatty acid	400
Rosin modified phenol-formaldehyde resin	100
Polymerized linseed oil	100

Yellow.—A concentrated paste obtained by blending the following ingredients was dispersed in the same carrier liquid as above.

A yellow pigment having the following formula



A varnish obtained by cooking rosin modified phenol-formaldehyde resin with linseed oil..... 800 mg.
Polymerized linseed oil..... 100 mg.
Any toner image softened at 80° C.

The heat-sensitive tape used in Example II was again employed and the transfer of the multi-colored image was accomplished at 80° C. The toner image bearing tape was laminated on baryta paper.

What is claimed is:

1. An electrophotographic process comprising; forming an electrostatic latent image on a photoconductive insulating layer, developing said latent image with a liquid developer comprising a finely-divided charged toner dispersed in an insulating liquid, pressing on the resulting toner image a heat-sensitive adhesive coating of a heat-sensitive tape comprising said adhesive coating and a flexible support, peeling off said tape from the layer with said toner image transferred onto said adhesive coating, and finally laminating said tape onto a final support to fix said image thereon, which is characterized by:

- (i) the toner image formed by the liquid development containing a thermoplastic heat-softenable resinous

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material the softening point of which is less than 90° C.;

- (ii) the softening point of said thermoplastic resinous material being lower than those of the heat-sensitive adhesive coating and also of the photoconductive layer;
- (iii) the transfer of said toner image onto the heat-sensitive coating being carried out at a temperature under which the toner image softens while the softening of the heat-sensitive coating does not substantially occur; and
- (iv) the lamination of the tape bearing the toner image on the final support being effected at a point where the heat-sensitive adhesive coating sufficiently softens where either said flexible support and/or said final support are transparent.

2. A method claimed in claim 1, wherein the adhesive tape comprises a transparent plastic film selected from polyethyleneterephthalate, polypropylene, and cellulose acetate.

3. A method claimed in claim 1, wherein the photoconductive coating comprises photoconductive ZnO and a resinous binder.

A method of claim 1 wherein the photoconductive coating contains a hardened thermosetting resinous binder.

5. A method of claim 1 wherein the heat-sensitive adhesive coating of the adhesive tape softens at a temperature from 70° to 100° C.

6. A method of claim 1 wherein the final support is a transparent plastic film.

7. A method as in claim 1 where the image obtained from the development of said latent image is a continuous tone image.

References Cited

UNITED STATES PATENTS

2,843,084	7/1958	Hayford	118—637
2,990,278	6/1961	Carlson	96—1
T 879,009	10/1970	Staudenmayer	96—1.4
2,297,691	10/1942	Carlson	96—1
3,275,436	9/1966	Mayer	96—1
2,965,482	12/1960	Dessauer	96—1

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