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3,704,119

ELECTROPHOTOGRAPHIC PROCESS USING TONER OF SAME REFRACTIVE INDEX AS ORGANIC PHOTOCONDUCTIVE LAYER

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No Drawing. Filed July 31, 1970, Ser. No. 60,116
Claims priority, application Japan, Aug. 7, 1969,
44/62,016

Int. Cl. G03g 13/08, 13/22

U.S. Cl. 96—1 R

7 Claims

ABSTRACT OF THE DISCLOSURE

A method for making electrophotographic reproductions which comprises the first step of forming an electrostatic latent image on an organic photoconductive layer which includes component materials of substantially equal reflective indices, and which includes light scattering inner surfaces homogeneously throughout its thickness or near the surface of the layer whereby the layer has an opaque appearance. The latent image is then developed according to any of the known electrophotographic development procedures, thus converting the latent image into a toner image, which decreases the light-scattering property of the organic photoconductive layer when impregnated into the layer. The toner deposited area of the layer is then made more transparent than the remaining areas by the action of heat and/or a solvent for the toner.

This invention relates to a new electrophotographic process utilizing organic photoconductors. Organic photoconductors which include polymerized materials having film-forming property by themselves and low molecular weight ones capable of forming solid solutions with other film-forming materials can provide very attractive recording materials in which the recording layer is optically transparent.

When an organic photoconductive transparent layer is formed on a suitable transparent or semi-transparent support such as cellophane, moisture-proof cellophane, tracing paper, various plastic films having thereon a conductive sub-coating, etc., the resulting material is conveniently used to produce electrophotographically a transparency, which is quite useful as a lantern slide for projection, a master for an overhead projector, or for contact printing material such as diazo paper or diazo film.

According to the conventional manner of practice, however, only an optically positive image has been easily obtainable in which the image area is opaque with a highly transparent background.

The present process is such as to provide a negative transparency utilizing organic photoconductive layers specially prepared.

The present invention comprises; forming an electrostatic latent image on an organic photoconductive layer which comprises components of substantially equal refractive indices, and which includes light scattering inner surfaces homogeneously dispersed throughout its thickness or near the surface of the layer, thus having an opaque appearance, developing said latent image according to any of known electrophotographic development procedures, thus converting the image into a toner image, said toner image being capable of decreasing the light-scattering property of said layer when impregnated into said layer, and then making the toner deposited area of the layer more transparent than the remaining areas.

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The organic photoconductive layer which comprises components of substantially equal refractive indices comprises either a single transparent component or plural components of nearly equal refractive indices.

The toner image comprises resins or organic compounds capable of melting or dissolving by heat or solvent and having refractive indices nearly equal to that of the photoconductive layer.

Practical methods of forming a light-scattering recording layer include the following:

(i) Incorporation of an ingredient not perfectly compatible with the organic photoconductor results in an opaque dry film. The degree of opacity can be controlled by selecting the solvent composition and drying conditions. This method is suited for an organic photoconductive polymer having a film-forming property by itself in which case the incompatible ingredient may be a polymer plasticizer or thermoplastic polymeric material which can form a clear or homogeneous solution with the photoconductive polymer. With such combinations, formation of light-scattering microscopic inner surfaces proceeds along with the evaporation of the coating solvent.

(ii) Utilization of a solvent composition the dissolving power of which becomes progressively weaker for certain or all of the components of the film-forming ingredients as drying proceeds often provides an opaque dried film as the result of phase separation. This method is applicable either for compositions containing an organic photoconductor having film-forming property, or for those comprising a low-molecular weight organic photoconductor and a film-forming polymeric material. In both cases, the solvent system may be selected so as to meet the above described requirement. One practical method is to use a mixture of a highly volatile, good solvent and a poor one of a higher boiling point (having a slower evaporation rate than the former) for the polymer to be dissolved. Another typical method is to utilize the so-called phenomenon "blushing" by employing a solvent system containing a water-miscible, highly volatile solvent such as lower alkyl alcohols, or ketones, coating the coating mixture and carrying out drying of the mixture in a relatively humid atmosphere whereby the moisture condenses onto the coated liquid film due to the heat of evaporation of the rapidly evaporating solvent, causing a phase separation of the film-forming material.

(iii) Technique of foam coating can be applied to the present purpose; one can prepare a W/O type emulsion by dispersing colloidal droplets of water in a water immiscible organic solution of an organic photoconductor; such emulsion is coated on a support to form a photoconductive coating and then subjected to heating in such a manner as to evaporate the water contained in the droplets. The resulting coating includes finely-divided air bubbles distributed throughout the coating. Further explanations will not be necessary except that the continuous phase of the emulsion should be composed of a water-insoluble material dissolved in a water-immiscible solvent.

Still other methods to provide a light-scattering, opaque recording layer are as follows:

(iv) A mixture of a low molecular weight, crystalline organic photoconductive compound and a resinous binder is dissolved in a suitable solvent, and applied onto a support. As the solvent evaporates, the photoconductive compound crystallizes to form a desirable opaque coating.

(v) In the method (iv), a photoconductive binder may be used.

(vi) In the method (iv), a non-photoconductive crystalline compound and a photoconductive polymeric binder may be used.

(vii) Utilization of two or more kinds of organic photoconductors which are compatible in solutions but lack in sufficient affinities with each other so as to form a clear film.

(viii) Light-scattering structure may be introduced only at the surface portion of the coating. For this purpose the following procedure may be employed; An organic photoconductive coating is formed in a transparent dried form by an ordinary manner, then on the coating is applied a uniformly small amount of solvent which are described in (ii), and again dried. By selecting a suitable drying condition, the surface portion in which the solvent penetrated becomes to include light-scattering inner surfaces.

A light-scattering photoconductive coating obtained by any of the above-described methods is processed according to known electrophotographic operations; in case of the Carlson process, the coating is uniformly charged under subdued light, exposed to an optical image to provide an electrostatic latent image and then developed by applying a toner to convert said latent image into a visible one and finally a toner image is obtained on such coating. Any other processes than Carlson method which utilize the photoconductivity of the coating and produce a toner image are all applicable for the present invention.

A thermoplastic, transparent, finely-divided resinous material is especially adapted for the toner of the present invention. Among such materials those which are soluble in some suitable solvents having a low boiling point or which have relatively low melting points are most preferred, since the present method requires the toner to easily permeate into the recording layer in order to diminish the inner surfaces. Thus, toner materials which become flowable or mobile upon heating or can dissolve in a solvent are especially preferred.

Practically most of resinous materials conventionally used for electrophotographic toner meet these requirements; suitable materials include polystyrene, poly(α -methyl styrene), styrene copolymers, cumarone-indene resin, petroleum resin, phenol-formaldehyde resin, rosin and its derivatives, xylene-formaldehyde resin, etc.

Development by electrophoretic process makes it possible to utilize more various kinds of materials as toner such as vinyl polymers, or cellulose derivatives, which are difficult to damage mechanically.

There may be two mechanisms for the phenomena of destruction of light-scattering structure by permeation of a toner therein, one in which the toner fills microscopic air voids in the coating, decreasing the difference of the refractive indices at the interface, and the other in which the toner acts as a solvent to dissolve the originally mutually incompatible ingredients.

It depends on individual cases which of these mechanism one can expect to occur. Whatever the theoretical background may be, a quite simple operation can practically produce a reversal image.

Permeation of the toner into the recording layer can be promoted by heating the layer to a point higher than the melting point of the toner. To realize a selective clearing of the toner-deposited area by heating, the softening point of the layer must be sufficiently higher than that of the toner used.

Another preferable method of promoting toner permeation is to subject the developed material to a solvent vapor which dissolves the toner but exerts no effect on the layer. This method is considered better than the former since the viscosity of the dissolved toner becomes quite low so that it can permeate into the layer very quickly.

Techniques as for providing a light-scattering coating are disclosed in the following patent specifications and it is quite easy for those skilled in the art to apply these techniques to the systems containing organic photoconductors. U.S. Pat. 2,939,802, U.S. Pat. 2,962,382, U.S. Pat. 3,020,172, U.S. Pat. 3,031,328, U.S. Pat. 3,194,677,

U.S. Pat. 2,961,334, and Japanese patent publication Sho 35/7879.

Typical examples of organic photoconductors are disclosed in the following examples;

Low molecular weight photoconductive compounds,

- (1) Oxadiazols—U.S. 3,189,447
- (2) Thiadiazols—U.K. 1,004,927
- (3) Triazols—U.S. 3,112,197
- (4) Imidazolones—U.S. 3,097,095
- (5) Oxazols—U.K. 874,634
- (6) Thiazols—U.K. 1,008,631
- (7) Imidazols—U.K. 938,434
- (8) Pyrazolines—U.S. 3,180,729
- (9) Imidazolidines—Belgium 593,002
- (10) Pyrazines—U.K. 1,004,461
- (11) Triazines—U.S. 3,130,046
- (12) Oxazolones—U.S. 3,072,479
- (13) Quinoxalines—Belgium 640,264
- (14) Quinazolines—U.K. 943,606
- (15) Furanes—U.S. 3,140,946
- (16) Acrydines—U.S. 3,244,516
- (17) Carbazols—U.S. 3,206,306
- (18) Phenothiazines—U.K. 980,880

25 Polymerized photoconductive compounds.

- (1) Polynucleus aromatic vinyl polymers—U.S. 3,162,532
- (2) Vinyl polymers having heterocyclic nucleus side chains—U.S. 3,037,861 and U.K. 964,871
- (3) Charge-transfer complexes between polymeric materials and Lewis acid—U.S. 3,408,187, U.S. 3,408,188, U.S. 3,408,189, U.S. 3,408,190

Images obtained by the present method on transparent supports can be used as lantern slide or projection film for projectors, and those on colored opaque supports appear positive with the exposed color of the supports. When the present method is carried out with a material comprising a support having highly light-reflective surface and a recording coating provided on said surface, the toner-deposited area looks brilliant by light reflection from the exposed support surface against dark background.

EXAMPLE 1

67 parts by weight of polyvinylcarbazole and 33 parts by weight (hereinafter part will always be given by weight when otherwise mentioned) of a polyester type polymer plasticizer "Plasticizer P.N." from Daihachi Chemical Industries were dissolved in a suitable amount of benzene. The resulting solution was coated on the metallized side of polyethylene-terephthalate film purchased from Toyo Rayon under the trade name "Metalmu" having a thickness of 90 microns. The coating and drying was carried out under an atmosphere of 50% R.H. During drying the two components which are substantially incompatible with each other were separated to form a white opaque coating. The dry thickness of the coating was about 8 microns.

After complete volatilization of solvent from the coated photoconductive coating, the member was uniformly electrostatically charged in subdued room light to a positive polarity. The uniformly charged member was then projected a light image transmitting a negative image on a microfilm to produce an electrostatic latent image, and immediately thereafter developed with a cascade developer comprising nitrocellulose coated glass beads and a finely-divided powder of a petroleum hydrocarbon resin having a melting point of 80° C. Since this powder was triboelectrically charged positive in the mixture, the so-called reversal development occurred. The member bearing the toner image was left in a closed vessel saturated with acetone vapor for a few minutes. Then the coating became clear at the toner-deposited area exposing the reflective gray color of aluminum underlying the coating.

The thus produced image was irradiated by light, and the reflected light was focused on an opaque screen on which appeared an image comprising brighter image areas and a dark background.

While the member was in acetone vapor, the background equally cleared but became again opaque after the evaporation of acetone.

EXAMPLE 2

50 parts of N-vinylcarbazol and 50 parts of polystyrene were dissolved in benzene. The solution was applied on a subbed surface of polyethyleneterephthalate film. The sub-coating was transparent and electroconductive. During evaporation of solvent crystallization of vinylcarbazol proceeded to give an opaque coating with 10 micron dry thickness. The dried film was positively charged and exposed to a photographic positive with line image to form an electrostatic latent image.

A cascade developer comprising ethylcellulose coated natural silica sand and finely-divided rosin which assumed a negative charge was used as developer and a positive reproduction of the original image resulted.

By subjecting the developed film to methanol vapor, the image area became transparent.

EXAMPLE 3

To 15 parts of toluene containing 2 parts of zinc salt of resin acid available under the trade name "Elkazit 165" (melting point, 150 to 170° C.) dissolved therein was added 0.004 part of crystal violet dissolved in a small amount of methanol. To the resulting solution 0.5 part of polymethylmethacrylate dissolved in 15 parts of acetone was further added. This mixture was used to prepare a recording material in the same manner as in Example 2. Drying was carried out by supplying a cold air stream of 60 to 70% R.H. on the coated film, whereby blushing of the coating took place leaving a light-scattering opaque coating.

An electrostatic latent image obtained by uniform charging and image exposure was visualized by magnetic brush development utilizing low melting point petroleum resin (melting point 70° C.) Heating of the developed member to 80° C. caused the toner-deposited area to change transparent.

EXAMPLE 4

An electrostatic latent image of positive polarity was formed on the member prepared in Example 2, and developed by a liquid developer comprising isoparaffinic carrier liquid and finely-divided polyvinylacetate dispersed in said liquid. Since this toner charged positive so-called reversal development took place. Exposure of the developed member to methanol vapor resulted in clearing of the toner-deposited area.

What is claimed is:

1. An electrophotographic method comprising electro-photographically forming a toner image on an organic photoconductive layer which consists essentially of at least one ingredient of a first refractive index and which includes light-scattering surfaces within the layer uniformly dispersed throughout the total thickness of the layer or near the surface portion of the layer, permeating said toner material which consists essentially of a transparent material which has a refractive index substantially equal to said first refractive index into said layer by the action of heat and/or solvent for said toner and thus decreasing the opacity of the layer only at the toner-deposited area.

2. The method claimed in claim 1 wherein said organic photoconductive layer is applied on a support of electroconductive transparent plastic film.

3. The method claimed in claim 1 wherein said toner material is polystyrene, poly(α -methyl styrene), styrene copolymers, cumarone-indene resin, petroleum resin, phenol-formaldehyde resin, rosin or its derivatives or xylene-formaldehyde resin.

4. The method claimed in claim 1 wherein said organic photoconductive layer includes air voids dispersed therein and where said toner, after permeating said layer fills said air voids.

5. The method claimed in claim 1 where said toner, after permeating the layer, selectively dissolves said layer at said toner deposited areas.

6. The method claimed in claim 1 where said toner material is a transparent resinous material.

7. The method claimed in claim 1 where said organic photoconductive layer comprises at least two ingredients, each having a refractive index substantially equal to that of said first refractive index.

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U.S. Cl. X.R.

96—1.5, 35; 117—17.5