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**COLOR ELECTROPHOTOGRAPHY EMPLOYING
DYE TRANSFER FROM A DYE-CONTAINING
PHOTOSENSITIVE LAYER TO AN IMAGE RE-
CEIVING SHEET**

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No Drawing. Filed Apr. 26, 1967, Ser. No. 633,724

Claims priority, application Japan, Apr. 26, 1966,

41/26,494

Int. Cl. G03g 13/22

U.S. Cl. 96—1.2

6 Claims

ABSTRACT OF THE DISCLOSURE

A process for the formation of a color image by forming an image of a water-insoluble toner on a layer consisting of a water soluble dye, photoconductive ZnO powders and a water-insoluble binder and bringing the image-bearing layer into contact with a dye receiving layer of moistened gelatin whereby the dye in the layer of the portions having no toner images is absorbed in the gelatin.

BACKGROUND OF THE INVENTION**(1) Field of the invention**

This invention relates to a novel color electrophotographic process.

(2) Discussion of the prior art

According to the earliest process of color electrophotography, reproduction of multicolor images could be accomplished by successively transferring toner images of different colored powders from the photoconductive surface to another surface. Briefly, this type of process comprises exposing a photoconductive plate, first, to an original. Exposure is made through light filters which enable one color to be recorded. Then the latent image is developed with colored toner to produce a copy of that color. This is repeated from each other color and the toner images are superimposed on the same copy sheet in register.

More recently, an improved method has been devised in which a panchromatically sensitized electrophotographic member is subjected to repeated cycles of charging, exposure, and development. In this method, it is required that after each development, the toner deposited area and the non-image area should exhibit substantially equal electrophotographic properties as for acceptance potential, dark and light decay rates. If the toner-deposited area exhibits the same acceptance potential as the non-imaged area, but a slower response to light, the image area will be covered with another toner at the subsequent development. On the other hand, if the toner deposition lowers acceptance potential, mixing of colors will become difficult. Such disadvantages can be overcome by the use of a developing agent which is photoconductive itself, so that it may act similarly to the sensitive layer. Many patents have been granted on this development process. Images obtained by any of these methods generally consist of fine particles and compare unfavourably with color images obtained by the use of the ordinary silver halide emulsion with respect to appearance, in particular, and reflection from the surfaces of the particles. A resin solution may be finally coated over such images so as to overcome this disadvantage.

SUMMARY OF THE INVENTION

It is an object of the invention to provide a novel and improved color electrophotographic process.

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It is another object of the invention to provide a novel electrophotographic sensitive layer suitable for practising the present process.

It is a still further object of the invention to provide an electrophotographic process whereby the transfer of a toner image can be eliminated.

This invention is concerned with an improved color electrophotographic process whereby substantially colored fine particles are not included in a final color image.

The feature of the color electrophotographic process of the invention lies in utilizing a photoconductive insulating layer or electrophotographic sensitive layer containing a dye in a form to be transferred to another dye-receiving sheet under suitable conditions and in a quantity sufficient to give suitable optical density after said transfer. Then an image is formed electrophotographically from a material capable of completely or partially suppressing the transfer of said dye to said dye-receiving sheet. The image bearing sensitive layer is then brought into intimate contact with a suitable sheet and the dye is transferred there-to under the action of a solvent for the dye. In this way there is obtained a reversal image of the electrophotographically formed image.

DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention will now be illustrated in detail concerning the steps involved and materials employed.

A uniformly mixed layer of photoconductive powder and insulating binding agent is particularly suitable for use as an electrophotographic photoconductive layer, since it is difficult to incorporate a large amount of a dye, for example, in a photoconductive selenium film prepared by vapor deposition. Zinc oxide or cadmium sulfide, for example, is preferably mixed with a dye powder and binding agent. A light-sensitive layer, formed by blending (mixing) the powder, in particular, zinc oxide with a binding agent, is sufficiently porous, so that a liquid which does not dissolve the binding agent, such as water or alcohol, when contacted with said layer, may thoroughly permeate it to a considerable depth without damaging it. If the composition of the photoconductive layer is enriched with photoconductive powder or if a suitable condition is chosen for preparation of the coating solution, the components soluble in said liquid are readily dissolved and taken out of the light-sensitive layer. This is considered to be substantially the case where the binding agent consists essentially of a strongly hydrophobic polysiloxane resin. Although any variety of binding agents may be used which are used for the ordinary electrophotographic light-sensitive layers, an alcohol-insoluble binding agent is preferred of course when the dye is soluble in alcohol. Similarly, when using an oil-soluble dye, the binding agent is hardened after coating or suitably processed so that it is not dissolved in a solvent used for the transfer of the dye.

The present invention is applicable to a light-sensitive layer utilizing a photoconductive organic compound. A number of dyes may be used for the light-sensitive layer. Water-soluble dyes are often used, due to the fact that a transfer solvent consisting essentially of water is naturally employed in the case of using a mordanted gelatin in the sheet to be dyed. This is typical of the invention. When selecting a cyan dye, as a water-soluble dye, it is desirable that the electrophotographic sensitive layer have a sensitivity in the red region of the spectrum, and the cyan dye may have a sensitizing action on a photoconductive material. This is the same for the other colors. The amount of the dye used in the invention is approximately 10–100 times as much as, for instance, a sensitizing dye incorporated in the electrophotographic light-sensitive layer of the prior art. That is, the dye of our invention is preferably incorporated in a proportion

of 0.5-5 parts by weight to 100 parts by weight of the zinc oxide. The sensitizing dye is in a proportion of 0.0005-0.05 part by weight to 100 parts by weight of zinc oxide in many cases. Therefore, if such large amount of dye is dissolved in a solvent and then added to a light-sensitive layer, a very intense color will be imparted to the resulting layer, but it is not always necessary to incorporate the dye in a dissolved form for accomplishing the objects of the invention. The dye may be used in the form of fine particles. Thus, in the case of mixing a binding agent and photoconductive powder with a solvent for said binding agent, the dye may be added and mixed in the form of fine particles and a solvent for the dye is preferably excluded.

Since it is often desirable that a layer containing a cyan dye have sensitivity in the red region of spectrum, as mentioned above, a sensitizing dye is also added additionally when the dye to be transferred has no or insufficient sensitizing action to the photoconductive material. It matters little whether this sensitizing dye is transferred during the step of transfer or not, because its amount is slight and it exhibits a hue like cyan. Where the transfer of the sensitizing dye is undesirable for some reason, for example, because the sensitizing dye is only slightly mordanted, it may be selected from dyes not soluble in the transfer solvent. Using water for the transfer, it may be selected from water-insoluble merocyanines, cyanine dyes and alizarine dyes.

The characteristics of an electrophotographic layer are effected by the presence of a water-soluble dye in a large amount. In particular, the insulation property thereof is worse at high humidity. A satisfactory layer can be prepared, however, by using a binding agent such as a silicone resin, whose resistance is scarcely lowered by humidity.

Employing well known means to lengthen the dark attenuation is also effective. A so-called oil-soluble dye which is insoluble in a polar solvent may be used so as to eliminate this problem. In this case, a toner and binding agent must be selected or combined so that they are not attacked by the transfer solvent.

As a support for the light-sensitive layer, a transparent film, such as polyethylene terephthalate, polycarbonate, polyethylene, polypropylene, polystyrene or cellulose derivatives, provided with a thin metal layer, is preferably used considering the registration in color reproduction, but other materials, such as paper, cloth and metal foil may be used.

The composition of the light-sensitive layer may be either uniform or varied in the direction of the thickness. For example, a large amount of dye may be incorporated therein near the surface, while there is incorporated no dye in the part in direct contact with the support. This serves to eliminate the waste inasmuch as only the dye of the surface is utilized and that of the interior is not utilized. The composition of the layer may be varied at other points so as to improve its characteristics. A porous layer may be provided on the surface, which is excellent for the electrophotographic characteristics and thin enough not to hinder the transfer of the dye. Another layer containing the dye may be provided under the porous layer. This serves to eliminate the problem that the resolution of the dye is too rapid to process without hindrance of the succeeding transfer step. In this case, only a sensitizing dye may be added to the surface layer.

The dye of our invention may be selected from the group used in the so-called "dye transfer process" as one to be transferred by water and fixed by a mordanted gelatin. As cyan dyes, for example, there are known Color Index Acid Blue-45, Acid Green-3, Acid Green-16, Acid Green-1 and Acid Blue-1, as magenta dyes are known Color Index Acid Red-80, Acid Red-34, Acid Red-1, Acid Violet-9, Acid Violet-12 and Acid Violet-19, and as yellow dyes are known Color Index Acid Yellow-23, Acid Yellow-11, Direct Yellow-12 and Acid Yellow-34. When not using a mordanted gelatin, many other dyes may be

employed, and all dyes will be employed if soluble in suitable solvents.

An image resistant to dye transfer is produced by the ordinary toner image. The material of the image must be resistant to solvents used for the transfer. That is to say, it is required to act as a stable resistance to dye transfer during that step. A typical material consists mainly of a water-insoluble thermoplastic resin. It is only of a secondary importance whether or not it contains coloring matter. Two cases are considered, first, where the image acts as a physical hindrance and second, where it consumes the dye. In the latter case, it may be a resin or powder which tends to be dyed with the dye. For an acidic dye, in particular, a basic resin or powder or composition containing one or more of them is effective.

Since the ordinary toner suppresses completely the transfer of a dye, a half-tone screen process must be used for reproduction of a continuous gradation. It may not be used in a case where the image is porous or consumes the dye. If the toner deposits in excess, the uniform contact of the light-sensitive layer and the sheet to be dyed is hindered and some disadvantages often occur in the dye transfer. Therefore, it is necessary to suitably control the quantities of toner deposition. The magnetic brush development may aid in preventing the excess deposition of the toner. Moreover, the so-called ferrotype may be applied to reduce the height of the toner. All of the methods for obtaining toner images electrophotographically are available for use in the invention. Further, methods of giving high quality images by utilizing a fine powder, such as a powder cloud or liquid developer may be used. The image may be fixed or not prior to dye transferring. Hydrophobic polymer grains, metal powder, water-insoluble inorganic compound, organic compounds, metal soap and glass powder act as simple inhibitors of dye transfer.

It will be understood from the foregoing illustration that when it is desirable to reproduce a multi-color image in accordance with the invention, three electrophotographic sensitive layers are provided containing cyan, magenta and yellow respectively and having light sensitivity at least to the red, green and blue region of spectrum respectively. The layers are charged electrostatically and then exposed through a color negative, as an original, with superimposition of a red, green and blue filter thereon respectively. If necessary, a screen may also be used together. Each material is developed with a toner. This is the normal developing wherein a toner of opposite polarity adheres to an area where an electrostatic charge of one polarity remains. The toner may be the same or different for the three materials. Thus, the toner image is left negative as it is. At the same time, the negative exposure is such as to give a mirror image of the final image, of course.

All of three or four primary color images constituting a final multi-color print may be prepared by the present method. However, one or more of the images may be formed by other procedures, such as; the conventional dye transfer process, or another electrophotographic dye transfer process of our invention.

The dye-receiving layer of the receiving member for water-soluble dyes comprises, most preferably, gelatin, glue, or casein. Other materials such as the following may also be used: polyvinyl alcohol, maleic anhydride, copolymers of maleic acid and vinyl monomer, i.e., styrene, vinyl acetate, vinyl alkyl ether and vinyl chloride, these copolymers containing half ester or half amide of maleic acid, methyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, cellulose sulfate, regenerated cellulose, sodium alginate, polycrylic acid, polymethacrylic acid, these partial amides, polyvinylpyrrolidone, vinylpyrrolidone-vinyl acetate copolymer, polyacrylamide, vinyl acetate-crotonic acid copolymers and compatible mixtures among these.

It sometimes happens that the dye image thus transferred has mottles and this is usually caused by the un-

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even distribution of the solvent, such as water, between the hydrophobic electrophotographic layer and the dye-receiving surface. To overcome this difficulty, it is effective to use a porous dye-receiving layer having a high water-absorptive property. Such a layer may be prepared by incorporating a comparatively large amount of an inorganic pigment, such as BaSO₄, TiO₂ or SiO₂ in a hydrophilic film forming material.

In the case of incorporating an oil-soluble dye in the light-sensitive layer, the sheet to be dyed may be a layer of a composition capable of being suitably hardened, if necessary, and readily dyed with the oil-soluble dye. A number of materials are available for obtaining an image of one color, although it is hard to apply the technique of mordanting. For example, the conventional papers, unwoven cloths, polymer layer-carrying materials and the like may be used.

As is evident from the foregoing description, the present invention has the following features and advantages in summary:

(1) A multi-color print of excellent quality in terms of color fidelity and fastness to light can be produced through simpler and more rapid electrophotographic procedures than the conventional dye-transfer process. This eliminates the use of separation negatives, as well as gelatin relieves, which were necessary and prepared by hand in a time-consuming, complex procedure in the conventional dye transfer process.

(2) Compared with color-images obtained electrophotographically by the use of colored toners, the images of our invention have excellent color transparency and the color reproduction is carried out with more fidelity.

(3) The present method can obviate the empirically known difficulty in producing liquid developers including negatively-charged toner particles having acceptable electrophoretic properties, which must be used to obtain a positive print on a negatively charged ZnO electrophotographic coating from a color negative original. Extensive studies on liquid developers have proved that many kinds of finely-divided materials assume a positive charge when dispersed in highly insulating organic liquids. Therefore preparation of liquid developers having therein negatively charged colored particles of desired hue is extremely difficult.

(4) With the use of dry development, such as, cascade, magnetic brush, or powder cloud, for which developers having positively or negatively charged particles are rather easily available, positive dye images are prepared from any original, whether a positive or negative.

(5) A single type of toner can be used in preparation of separation negatives for the three colors, resulting in commercial advantages.

(6) Controlling of the characteristics of electrophotographic light-sensitive layers of the three varieties is relatively easy and more advantageous commercially than controlling the characteristics by the use of three different developing agents.

EXAMPLES

In order to illustrate the invention, the following examples are given wherein parts will be given by weight, if not otherwise mentioned.

Example 1

Three kinds of homogeneous mixtures of good consistency were prepared separately in a ball mill of porcelain.

Coating solution "A":		Parts
Photoconductive ZnO	-----	100
Silicone resin varnish (non-volatile 50%, xylene solvent)	-----	40
Polyvinyl acetate varnish (non-volatile 50%, ethyl acetate solvent)	-----	10
Cyan dye, Color Index Acid Blue-9	-----	2
Toluol	-----	40

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Coating solution "B":		Parts
Photoconductive ZnO	-----	100
Silicone resin varnish (non-volatile 50%, xylene solvent)	-----	40
Styrnated alkyd resin varnish (non-volatile 50%, toluene solvent)	-----	10
Magenta dye, Color Index Acid Red-1	-----	2
Toluol	-----	40
Coating solution "C":		
Photoconductive ZnO	-----	100
Silicone resin varnish (non-volatile 50%, xylene solvent)	-----	36
Polyvinyl acetate varnish (non-volatile 50%, ethyl acetate solvent)	-----	9
Yellow dye, Tartrazine Color Index Acid Yellow 23	-----	2

Each of these three mixtures was diluted with toluol and applied to a sheet of paper of 100 microns in thickness, subbed with a copolymer of maleic anhydride and vinyl acetate, to give a thickness of 15 microns on a dry basis. It is to be noted that all the dyes used herein are water-soluble but insoluble in the solvents used for the preparation of the coating mixtures, xylene, toluene and ethyl acetate.

The coated sheets were heated to evaporate all the volatile ingredients, and further kept in darkness for complete dark-adaptation.

In this example, three separation negatives were used which had been produced from a color positive. Of course, the original obtained by the use of a red filter was combined with a light-sensitive layer A containing the cyan dye and the others similarly. In developing, a positively charged toner was used in all cases. When utilizing the cascade developing method, the use of an area changeable contact screen is preferred during the exposure. The composition of the developing agent used herein comprises, for instance, 100 parts of glass beads coated with nitrocellulose and 1 part of a toner for the Xerox Flat Plate marketed by Fuji Xerox Co. Ltd. Then a negative image was obtained from the negative original. After heat fixing the resulting images, the three negatives were pressed to a wet gelatin layer mordanted with an aluminum salt in register.

When the photoconductive layer consisting mainly of zinc oxide was contacted with the gelatin layer, the water-soluble dye incorporated therein as fine particles was released to the side of the gelatin layer. Since the one side is hydrophobic unlike the conventional dye transfer method, it is preferred to use water in a somewhat large amount on the side of the gelatin layer and it is more effective to wet the gelatin layer prior to the dye transfer with a pretreatment bath of diethylene glycol and/or ethylene glycol and an acidic resin having a strong affinity to the zinc oxide layer in water. The three transferring steps were carried out without interruption and after each step, the gelatin layer was preferably wetted with the pretreatment bath. The dye contained as particles was rapidly dissolved in water and gave a positive image of uniform density in a toner-free area.

After the foregoing steps, a color image was reproduced. Toner images were formed on the above-described coatings with a liquid developer comprising a toner which had been prepared by mixing 2 parts of ethyl cellulose, 8 parts of polyketone resin and 2 parts of phthalocyanine blue upon heat melting, and kerosene as carrier liquid. In this case, the use of a development electrode gave an increase in developing speed and a decrease in edge effect. A development electrode suitable for liquid development is described in our preceding Japanese patent application No. 1,666/66.

Example 2

It was proved from the results of Example 1 that only about 30-40% of the dye incorporated in the coating layer was effectively transferred to the gelatin layer. Then,

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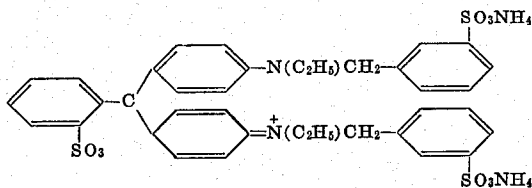
the following multi-layer sensitive material was provided in order to avoid the waste of dyes and to raise the dark attenuation property. A white sensitive layer comprising 100 parts of zinc oxide and 25 parts of an epoxy ester resin, obtained by reaction of epoxy resin, Epikote 1004, with the fatty acid of dehydrated castor oil, was formed on a sheet of paper to a thickness of 7 microns on a dry basis as a first layer. Then the coated sheet was heated at 60° C. for 4-6 hours to harden the resin. On this base each of the three coating solutions of Example 1 was then coated to 7 microns thickness on a dry basis, as a top layer. An excellent color image was obtained similar to Example 1.

Example 3

This example is characterized by cyan, magenta and yellow color forming layers having spectral sensitivity in the red, green and blue regions of spectrum respectively, whereby there is no separation negative required.

Coating solution "D": Parts	Parts
Zinc oxide -----	100
Silicone resin varnish (nonvolatile 50%, xylene solvent) -----	60
Toluol -----	40
Cyan dye, Color Index Acid Blue-9 (C.I. 242090) -----	2

The dye has the following structure and a sensitizing action to the photoconductivity of zinc oxide.



Coating solution "E": Parts	Parts
Zinc oxide -----	100
Silicone resin varnish (nonvolatile 50%, xylene solvent) -----	60
Toluol -----	40
Magenta dye, Color Index Acid Violet-6 -----	2.5

After preparation of the foregoing uniform solution, 0.02 part of Bromphenol blue dissolved in 5 parts of methyl Cellosolve was added dropwise thereto with stirring. This has a sensitizing action on the photoconductivity of zinc oxide and a peak of sensitization exists near 620 millimicrons. The sensitizing action trails a long skirt at the short wave length side and substantially covers the whole visible region. Acid Violet-6 lacks a sensitizing ability.

Coating solution "F": Parts	Parts
Zinc oxide -----	100
Silicone resin varnish (nonvolatile 50%, xylene solvent) -----	60
Toluol -----	40
Yellow dye, Color Index Acid Yellow-23 -----	2.5

After preparation of the foregoing uniform solution, 0.02 part of p-di-methylaminobenzylidene rhodanine dissolved in 5 parts of methyl Cellosolve was added thereto with stirring. This has a sensitizing action on the photoconductivity of zinc oxide, and exhibits a peak of sensitization near about 480 millimicrons and a sensitizing action up to about 600 millimicrons. Tartrazine scarcely exhibits a sensitizing property.

A color positive was obtained by using these three sensitized light-sensitive layers, exposing through a color

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negative as an original and a filter of red, green and blue respectively, and developing and transferring similarly. In the case of using a color positive film or conventional print as an original in place of the color negative, a negatively charged toner may be used, followed by reversal development. For example, the cascade or magnetic brush development is favourably carried out by a powdered natural sand or iron oxide coated with ethyl cellulose. In order to control the color balance, the toner image may be fixed by heating for a long time or by the use of a solvent. Such processing serves to raise the shield efficiency of the toner as well as to suppress the transfer of the dye through the softening of the thermoplastic resin in the light-sensitive layer by the solvent. Since an excessive deposition of a toner results in an incomplete contact between the light-sensitive layer and a gelatin layer, the toner amount is preferably limited to a certain extent.

Example 4

Parts	Parts
Zinc oxide -----	100
Oil Red (Color Index Solvent Red-24) -----	4
Silicone resin varnish (nonvolatile 50%, xylene solvent) -----	40
Toluol -----	20

The foregoing composition was blended in a ball mill of porcelain and applied to a subbed paper, as in Example 1, to a thickness of 10 microns on dry basis. After being negatively charged, a negative original of a line image was contacted thereon and exposed, over which a mixture of 100 parts of iron powder and 1 part of Xerox-914 Toner (Fuji Xerox Co. Ltd.) was applied thereby giving a negative image. After the image was fixed by heat, document paper wetted with ethanol was pressed thereon to obtain a positive image.

What is claimed is:

1. A process of forming a color image on a sheet which comprises producing a blanket electrostatic charge on a porous photoconductive insulating layer comprising a photoconductive material, an insulating film forming material insoluble in at least one of the group consisting of water, and alcohols and a dye soluble in at least one of the group consisting of water and alcohols where the material selected for said film forming material is insoluble in the solvent selected for said dye, said dye being incorporated in the porous photoconductive insulating layer, said sheet carrying a solvent for said dye when said sheet and light-sensitive layer are brought into surface contact, directing an optical image incident upon said charged

layer thereby producing on said layer a latent electrostatic image, applying a developer material, forming an image of said developer material on said latent electrostatic image, then bringing the image-bearing sensitive layer into close contact with said sheet whereby said solvent does not dissolve the image and light-sensitive layer but dissolves said dye, thereby transferring the dye in the light-sensitive layer to said sheet in a pattern corresponding to the presence or absence of the image.

2. The process of claim 1 wherein said photoconductive material is zinc oxide.

3. The process of claim 1 wherein said insulating film forming material is a hydrophobic polysiloxane resin.

4. The process of claim 1 wherein the surface of the sheet to be dyed is gelatin.

5. The process of claim 4 wherein said gelatin is wet with a water bath containing a lower alkylene glycol and an acidic resin having a strong affinity for said photoconductive insulating layer.

6. The process of claim 1 wherein a plurality of images are formed on each of a plurality of photoconductive insulating layers, each insulating layer containing a dye of a different color and transferring images of said different colors in registration to said sheet to be dyed, in accord-

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ance with the process of claim 1, to form a multicolor image on said sheet.

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U.S. Cl. X.R.

10 96—1, 1.6, 1.7, 1.8; 101—121, 149.1, 464, 470, 471