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DYE TRANSFER COLOR ELECTROPHOTOGRAPHY

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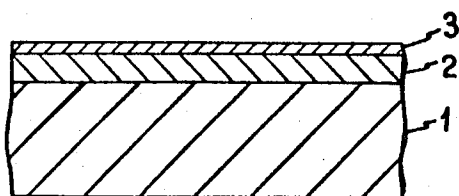


FIG. 1

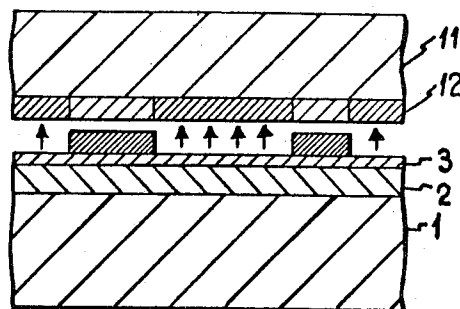


FIG. 4

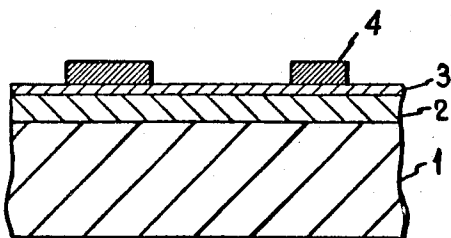


FIG. 2

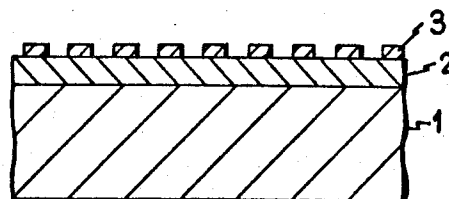


FIG. 5

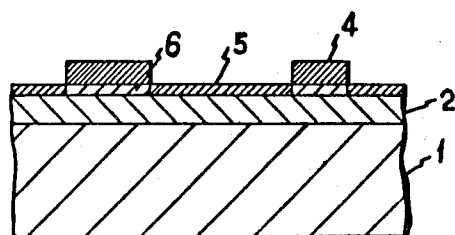


FIG. 3

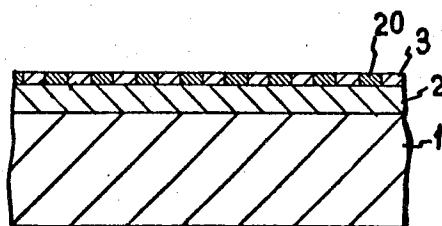


FIG. 6

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DYE TRANSFER COLOR ELECTROPHOTOGRAPHY
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6 Claims

ABSTRACT OF THE DISCLOSURE

A method of obtaining a color image which comprises, forming an image with an imaging material on a photoconductive electrophotographic member, the member having a surface comprised of a hydrophilic film-forming material which can absorb a dye dissolved in a polar solvent thereof, fixing the image, placing the image-bearing member in contact with a dye solution whereby the dye is absorbed in the surface, and then bringing the dye absorbed member into contact with a dye-receiving member whereby the dye is transferred onto the receiving member, thus obtaining a dye image, subject to the provision that the imaging material prevents the absorption of dye to the surface.

BACKGROUND OF THE INVENTION

The present invention relates to color electrophotography. More specifically, the present invention is concerned with a novel composition for a photoconductive coating and a method for the utilization of this coating for color electrophotography.

One of the earliest xerographic methods for the production of color images involved the utilization of an electrophotoconductive insulating layer and transfer of the desired image from this layer to a receiving member. This procedure is repeated a number of times using toners of various colors. In a more recently developed method, wherein a full-color image is produced on a panchromatically-sensitized photoconductive coating, toner transfer processes are not employed. Such a method involves subjecting the photoconductive coating containing the image of the first color, to subsequent procedures of charging, exposure, and development with toners of different colors, such as second and third colors. Accordingly to cause the production of a good quality full color image with such a process, it is important that the image and non-image areas exhibit equal electrophotographic properties, such as charge acceptance, and charge drainage rate in the presence of light.

Thus, if the image area has the same charge acceptance, but a slower response to light than the non-image area, the first color will be covered with other toners applied in subsequent developments, while if the image area exhibits a lower charge acceptance than the non-image area, reproduction of mixed colors will be difficult, thus resulting in a final print of a poor color quality.

SUMMARY OF THE INVENTION

It is, therefore, an object of the present invention to provide an improved composition and method for color electrophotography, which overcomes the above noted disadvantages.

Another object of this invention is to provide a method for color electrophotography without accomplishing transfer of a toner image.

A still further object of the present invention is to provide an improved composition for a photoconductive coating, suitable for use in color electrophotography.

The foregoing objects and others are accomplished in accordance with this invention by providing a novel

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method for color electrophotography which comprises the formation of an image on a photoconductive insulating coating with an imaging material, the photoconductive insulating coating containing a surface comprising a hydrophilic film-forming material which can absorb a suitable dye dissolved in a polar solvent thereof, the imaging material being able to wholly or partly prevent the absorption of dye to the surface, fixing the image, placing the image-bearing coating in contact with a dye solution whereby the dye is transferred onto the receiving member, thus obtaining a dye image. Briefly thus, the present method may be understood as a procedure of obtaining a matrix for dye transfer process by means of electrophotography.

The image bearing photoconductive member can be used as a matrix which may be subjected to repeated use. The matrix thus prepared proved to yield a number, generally forty or fifty or more, of dye prints by cyclic use.

The present method will be described more in detail with reference to the accompanying drawings in which: FIG. 1 shows the cross-sectional view of an electrophotographic member prior to formation of a toner image, comprising a substrate 1, a photoconductive insulating coating 2, and 3, an upper-most surface coating of a hydrophilic, dye-absorptive coating.

FIG. 2 illustrates a cross-sectional view of an electrophotographic member subsequent to formation of the image 4, while FIG. 3 illustrates a toner image bearing photoconductive member in such a state, that the surface layer thereof has absorbed a suitable dye at the non-image area 5.

FIG. 4 illustrates a dye-receiving member contacted with the image bearing and dye-absorbed photoconductive member, whereby the dye once embedded in the coating 3 is transferred to the dye-receiving layer 12, 11 being the support for 12, comprising suitable materials such as paper, plastic, metals, and the like. The composition of 12 resembles that of 3, the representative example being given as a gelatin coating. This coating may preferably be mordanted, by suitable mordanting agents.

Other electrophotographic members suitable for the present method are illustrated in FIG. 5 and FIG. 6, wherein the surface coating is provided in a form of isolated islands, or isolated with a more insulating material 20.

Illustrative examples of the suitable substrate material include paper, metal, glass, ceramics, plastic films, and the like, which must be more conductive than the photoconductive coating, to be provided thereon, at least at the surface contacting the coating. A sufficient conductivity is imparted to paper by impregnating with hygroscopic inorganic salts or antistatic organic compounds.

Paper substrates are sometimes scrubbed with suitable film-forming materials prior to the coating of a photoconductive layer so as to prevent the impregnation of the photoconductive coating mixture into the porous structure of the paper.

Photoconductive coating 2 may comprise thin homogeneous films of amorphous selenium, sulfur, anthracene, or polyvinylcarbazol, or intimate mixtures of photoconductive substances embedded in insulating resinous materials. Photoconductive substances used in combination with insulating resinous materials include finely-divided amorphous selenium, zinc oxide, cadmium sulfide, zinc sulfide, cadmium selenide, other photoconductive metal oxides, iodides, sulfides, selenide, telluride, or sulfoselenides.

Knowledge, or techniques to improve or control the electrophotographic properties of electrophotographic photoconductive coatings which are known to those

skilled in the art may all be applied for the coating used in the present method.

The surface coating 3 comprises a novel hydrophilic, water-insoluble film-forming material which can absorb and retain dyes which are soluble in highly polar solvents such as water. The most preferred coating is comprised of hardened gelatin, however other materials such as glue, casein, albumin, polyvinyl alcohol, maleic anhydride, or maleic acid with a variety of vinyl monomer such as styrene, vinyl acetate, vinyl alkylether, or vinyl chloride, copolymers of half ester, or half amide of maleic acid with vinyl monomers, corresponding metal salts of these, methyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, cellulose sulfate, regenerated cellulose, sodium alginate, polyacrylic acid, polymethacrylic acid, derivatives from these such as partial esters, partial amides, or salts, copolymers of acrylic or methacrylic acid, polyvinyl pyrrolidone, poly(vinyl pyrrolidone/vinyl acetate), polyacryl amide, poly(vinyl acetate/crotonic acid), and mixtures among these, may also be used.

It is important in the practice of this invention that the surface coating be insoluble in water after coating; its thickness must be as small as possible since an increase in the thickness inevitably causes deterioration of electrophotographic properties of the resulting member. The amount of dye absorbed in a unit area of the surface coating is proportional to the thickness of the coating, accordingly, a coating of uneven thickness results in a print exhibiting uneven density of dyes.

The surface coating should be firmly bonded to the underlying photoconductive coating, since a severe strain arises during the dye transfer procedure between these two coatings. The surface coating swells upon absorbing the solvent for the dye, while the underlying layer retains its original state because of its hydrophobic property. To eliminate this difficulty, in some instances a thin intermediate coating is provided between the two coatings. Copolymers including maleic anhydride generally improves the adhesion between the two coatings when incorporated in the coating 3.

A good adhesion can be brought about when a surface coating is applied on a photoconductive coating including a thermosetting resin binder before the binder is cured.

The image 4 behaves as a physical and chemical barrier against dye transfer, and it has been proved that conventional toners comprising thermoplastic resin and suitable coloring matters can completely prevent the transfer of dyes. The imaging material should not dissolve in solvent used for dye absorption and dye transfer. Therefore, hydrophobic resinous materials are most preferred; it matters little whether the material is colored or not.

With a toner image which completely prevents the penetration of dye therethrough, a final dye print having a tonal rendition can be obtained only by utilizing a screen or dot pattern of toner image. With an image which partly prevents the penetration of dye therethrough, the density of dye can be changed continuously.

When a toner image is raised from the level of the photoconductive surface, it becomes difficult to realise an intimate contact between the surface and the dye-receiving layer, which brings about an incomplete transfer of dye. Accordingly an excessive toner deposition should be avoided. Magnetic brush development is recommended because with this method of development an excessive toner deposition seldomly occurs. A toner image once obtained may be squeezed or pressed by applying heat and/or pressure on the photoconductive member, for example, by means of glazing roll.

Toner images may be prepared by any known methods of electrophotographic development, among which liquid development or powder-cloud development are preferred because of their ability to produce images of excellent

high quality. A toner image is ordinarily fixed before the dye transfer procedure, although this is not necessary. When an unfixed image is subjected to dye transfer procedure, the toner image may be damaged or transferred with the dye on the receiving member, whereby, however, by controlling working conditions it is still possible to carry out the dye transfer itself successfully.

In those instances wherein the photoconductive coating is active only at a certain fraction of the visible spectrum, for example, at near ultra-violet region, previously prepared three separation negative originals are needed. With a coating having a panchromatic response, a color negative may be used as an original utilizing three separation filters, upon exposure to a photoconductive member. If a set of member is available each of which exhibits a light response only at blue, green or red region of spectrum, even the filters are not necessary.

A wide variety of dyes are available for practicing the present invention, which include as cyan dyes, color index, acid blue 45, acid green 3, acid green 16, acid green 1, acid blue 1, as magenta dyes, color index, acid red 80, acid red 34, acid red 1, acid violet 9, acid violet 12, acid violet 19, and as yellow dyes, acid yellow 23, acid yellow 11, direct 12, and acid yellow 34, etc. These are preferably used because of their mordantability, which makes it possible to fix a dye in a dye receiving layer so as to inhibit lateral diffusion or reversal transfer of a dye onto a photoconductive member.

As will be understood from FIG. 3, the toner image is a reversal one relative to the final dye print. Accordingly, in general, to produce a color positive, a negative toner image may be provided electrophotographically from a negative color image. Besides, the toner image should be a mirror image (laterally reversed) as for the final print.

During dye transfer procedure the layers 3 and 12 tend to swell which causes a brittle, hard toner to crack or be separated from the coating 3. Therefore, toner materials having a strong affinity with the coating 3 as well as flexibility are required.

As is clear from the above explanations, the present method has the following novelties and advantages over conventional methods for obtaining dye images.

(1) A full-color image of an excellent color quality and fastness to light can be produced through simple and rapid electrophotographic procedures eliminating the use of separation negatives as well as gelatin reliefs which have been prepared through hand and time-consuming complex procedures.

(2) The resulting image has a better color quality than those obtained electrophotographically with the use of colored toner particles, especially in respect to color purity.

(3) The present method can obviate the known difficulty to produce 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 upon 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 wherein developers having positively or negatively charged particles are rather easily available, a positive dye image can be prepared from any of the original, a positive or negative.

(5) Only a single type of developer may be commonly used to prepare three separation toner images, which is a big advantage for practicing the present method on an industrial scale.

(6) It is more easily performed to control the electro-

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photographic properties of three different electrophotographic coatings than to control those of three different electroscopic developers.

(7) The present method does not include toner transfer procedure which tends to lower the image quality. A toner image comprising extremely fine particles such as those obtained by liquid development cannot be satisfactorily transferred without an elaborated apparatus.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example I

On a baryta coated paper a homogeneous mixture comprising 100 parts of photoconductive ZnO, 36 parts of epoxyester of dehydrated castor oil fatty acid (varnish, non-volatile content 50%), 20 parts of silicone resin varnish (non-volatile 60%), 0.1 part of cobalt naphthene, and 30 parts of toluol, was applied so as to give a thickness of about 15 microns on dry base. After toluol was evaporated, aqueous solution of gelatin containing formaldehyde was again coated on the ZnO layer. The thickness of this gelatin coating was about 2 microns after drying. Thus prepared member was maintained at 40° C. for 16 hours for complete curing of epoxyester resin.

At darkness the coated side of this member was negatively charged, and exposed to a light image through a separation negative produced from a color negative using red filter. A cascade developer including a toner comprising polystyrene and carrying a positive charge was applied on the exposed member. The resulting toner image was subjected to heat and further pressed against a heated metal plate whereby the fixed toner image was partly buried into the surface coating. The toner-image bearing member was then immersed in an aqueous solution of acid blue 45 (color index number) (0.02% concentration) for a while, then brought into contact with a gelatin coated dye transfer paper mordanted with aluminum salt. The contacted assembly was disassembled after 2 minutes. A cyan print was obtained on the mordanted paper.

Example II

To the coating mixture described in the above example was added $\frac{3}{1000}$ part of bromophenol blue in the form of methanol solution. The resulting mixture was coated on a baryta paper in a similar manner as in the above example. On the dried coating an aqueous solution of polyvinyl alcohol and Werner type chromium complex was applied to give a dried thickness of about 2 microns. The coated paper was kept in a hot atmosphere so that the curing of polyvinyl alcohol and binder in the photoconductive coating completed. The member exhibited almost panchromatic response to light. Three different sheets of this member were charged and exposed to light images transmitting a color positive original utilizing three separation filters (blue, green, and red). Three corresponding toner images were obtained. The developer used comprised of finely-divided terpolymer of vinyl chloride, vinyl acetate, and maleic anhydride (purchased under the trademark "Denkavinyl #1000C" from Denki Kagaku Ind.) dispersed in kerosene. In this liquid developer the toner assumed a negative charge, and the toner deposition occurred at the light-struck area. During development, a developing electrode was used, which was closely spaced from the image surface and applied with a negative voltage. The member bearing the image obtained by using red

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filter was imbibed with acid blue 1, the one from green filter with acid violet 6, and the one from blue filter with acid yellow 23, respectively. These three sheets were pressed in register to a dye receiving gelatin coated paper.

A color print was reproduced.

Other modifications and ramifications of the present invention would appear to those skilled in the art upon reading the disclosure. These are intended to be within the scope of this invention.

What is claimed is:

1. A method of obtaining a color image which comprises electrostatically forming an image with a toner material on an electrophotographic member comprising a photoconductive insulating layer having coated on the surface thereof a hydrophilic water insoluble film-forming material capable of absorbing a dye dissolved in a polar solvent, said film-forming material being substantially uniform in thickness, fixing said image, placing said image-bearing member in contact with a dye solution comprising a dye dissolved in a polar solvent whereby said dye is absorbed by said hydrophilic film-forming material of said electrophotographic member in those areas unprotected by said toner, said photoconductive insulating layer and toner material being insoluble in said dye solution and said toner material incapable of absorbing said dye, and bringing said electrophotographic member into contact with a dye receiving member whereby said dye is transferred thereto from said electrophotographic member in an imagewise configuration to produce said color image.

2. The process as disclosed in claim 1 wherein said film-forming surface coating is provided in the form of isolated islands.

3. The process as disclosed in claim 1 wherein a full color image is obtained by repeating the process steps as described utilizing at least two differently colored dyes whereby the images formed are printed in registration on said dye receiving member to produce a color print.

4. The process as disclosed in claim 3 wherein three separate toner images are formed sequentially utilizing blue, green and red filters with corresponding yellow, violet and blue dyes being stepwise absorbed by said film forming material and subsequently transferred in registration to said dye receiving member to produce said color print.

5. A method in accordance with claim 1 wherein the photoconductive coating is amorphous selenium, and the hydrophilic film forming material is hardened gelatin.

6. The method as disclosed in claim 1 wherein said toner material is a hydrophobic resinous material.

References Cited

UNITED STATES PATENTS

2,029,077	1/1936	Lejeune	101—149
2,455,735	12/1948	Condax	101—211
2,870,704	1/1959	Goldberg et al.	101—149.1
3,057,720	9/1962	Heyford	96—1
3,332,347	7/1967	Gundlach	101—469
3,357,830	12/1967	Bixby	96—1.2
3,386,822	6/1968	Brynko	96—1.4

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U.S. Cl. X.R.

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