

[54] **ELECTROPHOTOGRAPHIC PROCESS**

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[58] Field of Search **96/1, 1.2, 1.5, 1.8; 117/17.5, 37 LE**

[56] **References Cited**

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[57] **ABSTRACT**

An electrophotographic process which comprises uniformly charging a surface of a photoconductive insulating layer having light-sensitivity in an intrinsic sensitive region and extended spectrum region, the photoconductive insulating layer exhibiting light fatigue when exposed to light in the range of its intrinsic sensitive region, imagewise exposing the surface to light which covers the entire light-sensitive region of the light-sensitive layer from an original which includes a first colored portion which absorbs substantially all of the light and a second colored portion which absorbs from the light substantially only the wavelength range corresponding to the intrinsic sensitive region to form on the photoconductive insulating layer an electrostatic latent image corresponding to the first colored portion and a substantially non-conductive area corresponding to the second colored portion, developing the electrostatic latent image by electroscopic developer, again uniformly charging the surface of the layer to form a second electrostatic latent image at least at the substantially non-conductive area and developing the second electrostatic latent image with electroscopic developer.

8 Claims, 6 Drawing Figures

FIG. 1

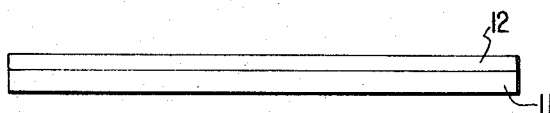


FIG. 2

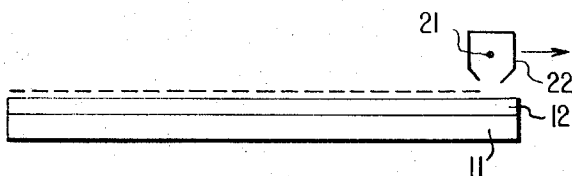


FIG. 3

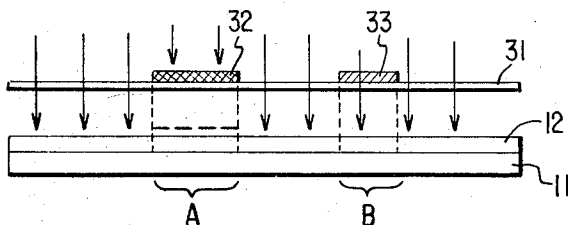


FIG. 4

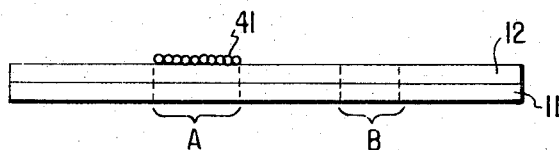


FIG. 5

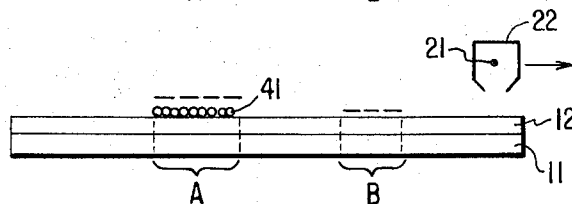
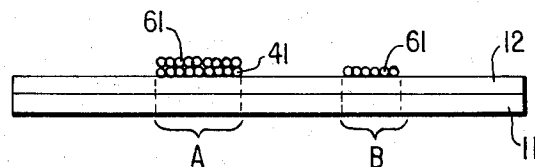


FIG. 6



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ELECTROPHOTOGRAPHIC PROCESS

DETAILED EXPLANATION OF THE INVENTION

This invention relates to a novel electrophotographic process. The method of this invention is particularly useful color copying.

An electrophotographic process in which electrostatic latent images formed on the surface of a photoconductive light-sensitive layer are developed with electroscopic powders (toners) has already been utilized practically. By the use of repetition exposure and development procedures in each color a copy of an original (object) containing color image is obtained. For example, a process containing imagewise exposure on a charged xerographic plate through a color separation filter, development by toners having complementary color to the color filter, and transfer the toner image onto a sheet of white paper is repeated changing the combination of the filter and toners to obtain a color image. And, so-called overprinting method comprising cycles of charging electrophotographic light-sensitive paper, imagewise exposing by color separation method and developing by color toner for obtaining color image has already been practically used as "REMAK PROCESS."

However, these methods have a disadvantage of requiring a long time. Namely, a procedure comprising charging - exposing - developing must be repeated at least twice to obtain a color image. Further, during the above procedure, there has been a problem of registration, that is a relative position of original and sensitive layer at the time of exposure must precisely be maintained. Because of these reasons, a rapid process for obtaining a color copy and machine therefor has not been developed.

Accordingly an object of this invention is to obtain rapidly a copy of color images. Another object is to obtain color images by one time exposing operation and further object is to obtain color images with accurate registration.

The inventors found a method to obtain a color image by only one time exposing operation.

Namely, the electrophotographic process of this invention is characterized in that a surface of a photoconductive insulating layer having light-sensitivity in intrinsic sensitive region and extended spectrum region is uniformly charged in the dark, imagewise exposing the layer with light which covers the whole sensitive region of the layer developing the formed electrostatic latent image with an electroscopic toner to form a first image charging again the entire surface of the layer then developing with an electroscopic toner to form a second image.

The method of this invention will be explained in more detail with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWING

FIGS. 1-6 are schematic views showing the process of this invention.

FIG. 1 shows a sensitive sheet comprising a photoconductive insulating layer 12 provided on a support 11. The photoconductive insulating layer, comprises a mixture of photoconductor such as zinc oxide, titanium dioxide, cadmium sulfide, or zinc sulfide, and insulative resin also a layer of an organic photoconductor and a layer containing an organic photoconductive material

may be used. A support 11 or its surface to be applied a sensitive layer 12 should be treated to show conductivity.

The sensitivity of a photoconductive material is normally limited to a spectral region where an intrinsic sensitivity of the material exists.

The intrinsic sensitive region of conventional photoconductors generally exists at ultraviolet region or near ultraviolet region. A photoconductor to be employed in this invention is preferred to be spectrally sensitized so that it would have photoconductivity to the light of range other than its intrinsic sensitive region. As a method of the sensitization, the commonly well known methods which employ a sensitizing dye gives preferably effects. The sensitive region may also be extended by the use of coloring pigments.

FIG. 2 shows an example of process for uniformly charging the surface of light-sensitive layer 12. 21 is a corona electrode and 22 is a conductive case. Corona electrode comprises fine metal wire or metal probe. High voltage of direct or alternative current is applied to the corona electrode.

FIG. 3 is a view showing image being exposed on the surface of the charged light-sensitive layer. Light comprising intrinsic sensitive region and spectrally extended sensitive region is being applied. In the case that a dye-sensitized zinc oxide is used as a photoconductor, light from a light source supplying near ultraviolet rays, for example a tungsten bulb or a fluorescent lamp is applied. 31 is an original. As the original, a black image 32 and a color image (other than black) 33 are beared on a transparent support is used.

An electrostatic latent image is formed on the sensitive layer 12 by means of exposure of light through an original. On portion A corresponding to black image 32 of the original the charge is retained since the portion was not exposed. An electrical charge on portion B corresponding to a color image 33 is discharged, as a part of light within the sensitive region of the sensitive layer reached the light-sensitive layer through a color image 33. During the exposure an important phenomenon has occurred in the sensitive layer 12. Namely, usual color images do not transmit or reflect the ultraviolet or near ultraviolet rays, therefore, the portion B corresponding to a color image 33 is not irradiated with the light of an intrinsic sensitive region of the light-sensitive layer. The portions other than A and B on the light-sensitive layer 12 is exposed to light of an intrinsic sensitive region and sensitized region.

When the photoconductive layer containing dye-sensitized zinc oxide is exposed to light of its intrinsic sensitive region, the photoconductive layer shows light-fatigue. The light-fatigue is exhibited as a persistence of conductivity after exposure. Accordingly, a portion A having electrostatic latent images and non-light fatigued portion B are formed on the light-sensitive layer 12 in FIG. 3.

FIG. 4 shows developing step of the electrostatic latent image formed according to the process as shown in FIG. 3 with an electroscopic toner. Only on the portion A where the electrostatic latent image existed the developing toner is electrostatically deposited. While the toner does not deposit on the non-light fatigued portion B where electrical charge was conducted away.

FIG. 5 shows a process in which the sensitive sheet having an image obtained along the method of FIG. 4 is subjected to recharging operation. The portions A

and B where has no light fatigue due to exposing operation of FIG. 3 are charged by this recharging operation. The portion effected with light fatigue (the portions other than A and B in the light-sensitive layer) is hardly charged or a little if any.

In the recharging operation, the charge on A and B portions is a little decreased at edge portions, as the first image previously formed and light-fatigued portion have already been generated on the light-sensitive sheet, therefore, an indistinct image may be obtained. In such a case an improved charging method described for example in the specification of British Pat. No. 1,177,593 is preferably employed. According to the method, corona charging is not performed directly but through an insulation layer.

FIG. 6 shows a process which the sensitive sheet is again developed. A toner 61 is deposited electrostatically on A and B portions. Accordingly the images thus formed on the light-sensitive sheet are, at A portion, an image comprising a mixed color of developing toner 41 and developing toner 61, and, at B portion, an image comprising only developing toner 61.

An electroscopic developer, those used in a conventional electrophotographic process such as cascade developer, magnetic blush developer, liquid developer, and powder cloud developer may be employed. It may also be possible to carry out development by utilizing wetability to a liquid at the latent image portion, as shown in U. S. Pat. No. 3,285,741.

Any organic or inorganic pigments, so far as they are used as toners in usual electrophotographic developing methods, may be used which is, for example, carbon black, brilliant carmine 6B, phthalocyanine blue, benzidine yellow, hanza yellow, chrome yellow, iron oxide, cadmium sulfide, and quinacridon red.

It is possible to determine colors of A and B portions by appropriate selection of toner 41 in the first developing process and toner 61 in the second developing process. Some examples of the color combination will be shown in the Table 1.

TABLE 1: Examples of combination of developer.

Example developing	Color of developer		Color of Image	
	The first	The second developing	A portion	B portion
1	black	magenta	black	magenta
2	black	red	black	red
3	black	cyan	black	cyan
4	green	magenta	black	magenta
5	black	green	black	green
6	cyan	magenta	blue	magenta
7	blue	red	purple	red
8	magenta	cyan	blue	cyan
9	yellow	cyan	green	cyan

Examples 1, 2 and 4 are suitable for copying an original which is a printed document having red correction marks and/or signature in red color. Example 3 is suitable for copying original which is a printed document in black having additional remarks or signature in blue ink.

It is apparent that a two-color copy may optionally be obtained by other combinations. The difference of color tone between A and B portions may be further emphasized by adding a material for preventing recharging to the developing toner of the first developing process.

According to the invention, in the case of using a colored paper on which letters, etc. are printed, as origi-

nal, the letters, as well as the color of the paper can, of course, be reproduced.

A developing method in the first developing step does not necessarily to be the same as that in the second developing step. For example, the first color developing step may be done by using a liquid developing method, and the second color may then be developed by cascade developing method.

However, both of the first and second developing steps may preferably done by a liquid developing method to obtain good results. Namely, fixing of the toners is easily performed, and while the sheet being still wet, after developing the first color, the recharging and the subsequent second color development steps may be carried out.

When the first color is formed by a liquid development while the second color is formed by a dry type developing method, it is necessary that the surface of the sheet be dried after the first development. If the sheet surface is still wet, it may cause to stick dry toners to non-image portions. An image having varied optical density due to the difference of color hue of the original may be obtained by using the same color toner in both the first and the second developing steps. As a light-sensitive sheet to be used in the process of this invention a layer may be appropriate which shows a light fatigue against irradiation of light of the intrinsic sensitivity region, but not to have light fatigue against the light of optically sensitized region. Examples of such materials may generally be found in a dye-sensitized zinc oxide sheet.

The dyes used in the invention for extending the spectral sensitivity of the recording sheet are well known in the art, and found, for example, in U.S. Pat. No. 3,052,540. The typical examples of dyes are fluorescein, eosine erythrosine, rose bengal, malachite green, crystal violet, fuchsine, methyl green, brilliant green, methylene blue, acridine orange, kryptocyanine, pinacyanol, alizarine red, etc. Also a method of dye sensitizing photoconductive zinc oxide powder with dye in combination with a Lewis acid as described in British Pat. No. 1,005,245 may be employed in this invention. The dyes used in the method are auramine O, thioflavine TG, rhodamine B, quinaldine red, nigrosine, 1,4-diaminoanthraquinone, chrome blue GCB, lithosol blue 6G, etc.

As a sensitizing dye for photoconductive titanium dioxide used in the invention there may be illustrated auramine, fluorescein, rose bengal, basic flavine 8G, etc. The amount of dye may readily be determined by a person having ordinary skill in the art.

The insulative resinous binder of the sheet may be selected from thermoplastic resins and thermosetting resins. Examples of suitable resins are vinyl chloride-vinyl acetate copolymers, polystyrene, styrene-butadiene copolymers, polyolefines, acryl resins, alkyd resins cured with metal salts or polyisocyanates, polyesters, etc. Preferred binder is copolymers of vinyl chloride and cured alkyd resins.

The ratio of the photoconductor to the resinous binder may be varied between 8 : 1 to 2.5 : 1 by weight.

In this invention the light-sensitive layer may be charged to either positively or negatively. When zinc oxide is employed as photoconductor, the sensitive sheet is ordinarily used by negatively charging, however, it may be utilized positive charging by using copolymers of vinyl chloride as binder. While titanium di-

oxide-binder sheet may be charged to both polarities.

Of course, a light-sensitive sheet which is difficult to be fatigued in its intrinsic sensitivity region while readily fatigued by light of sensitizing region may be employed in this invention.

In the process of the invention, it may be preferable that an electric charge on a light-sensitive sheet is opposite to that of a developing toners.

Accordingly, in the case of a sensitive sheet negatively charged as shown in the FIG. 2 a toner used in the step of FIG. 4 is preferred to be positively charged.

The same relation applies to the processes in the FIGS. 5 and 6. Also it is substantially possible to embody this invention by changing the polarity of the first and second charging according to the polarity of developing toner.

By means of the above description a novel electrophotographic process which can provide color images would be clear. Hereinafter described are examples of this invention, and the persons skilled in the art may easily understand that the following component, manufacturing method, and the procedures may be changed within the scope of the invention. Therefore the invention should not be limited only to the following examples.

EXAMPLE 1

The surface of a sheet of paper having a conductive layer has been provided with a photoconductive insulating layer comprising styrene modified alkyd resin hardened by polyisocyanate compound and photoconductive zinc oxide (Sazex made by Sakai Chemical Industry Co., Ltd.)

Weight rate of the resin and the zinc oxide being 4 parts by weight of zinc oxide per 1 part by weight of the resin. The sensitive region of this sensitive layer has been extended in the visual spectrum region in its entirety by adding sensitizing dyes of fluorescein, rose bengal and brilliant blue FCF.

The sensitive layer was sufficiently adapted to the darkness retained at 40°C., and its light fatigue was well removed. And then it was subjected in the dark for uniform charging to corona discharge from corona electrode given with -6KV. The surface potential was -210V. The original used was a white art paper typed with black ink having some additional remarks in red ink. The light from a white wolfram light source was applied to the original, and its reflective light image was projected to a surface of the charged sensitive layer.

After exposure, the surface of the layer was wetted with Isoper H (isoparaffinic hydrocarbon made by Esso Standard Co.) and then it was developed by black liquid developer dispersed with carbon black in isoparaffinic hydrocarbon. The charge of the toner was positive. Black image for only the typed portion in black in the original was obtained. Immediately after the development, the sensitive layer having a black image was again subjected to corona discharge from corona electrode having -6KV, and was then developed by a liquid developer having magenta color toner dispersed with Brilliant Carmine 6B. The toner of magenta color in the developer had positive charge.

Subsequent to the development, the entire surface was washed in Isoper E (isoparaffinic hydrocarbon, made by Esso Standard Co.), and was then dried. The additional remarks in red ink in the original was developed in magenta color on the sheet. As magenta color

was also deposited on the black image, the image turned out a little reddish, however, when its entire surface was lacquered, the black toner and magenta toner were mixed each other, resulting in almost pure black.

EXAMPLE 2

In place of the sensitive layer employed in Example 1 a sensitive layer comprising 10 parts by weight of zinc oxide per 1 part by weight of resin, was used. The other conditions are the same as for those of Example 1. The image obtained after development had fog of magenta color on its entire surface, the cause of which is presumed that the light fatigue of the sensitive layer was less than that of the sensitive layer used in Example 1.

EXAMPLE 3

In place of the original in Example 1, a sheet of red color paper printed with black ink was used as an original. The other conditions remain the same as those of Example 1. The sheet obtained had magenta toner deposited on its entire surface, in which a black image was clearly copied.

EXAMPLE 4

In place of the first black liquid developer of Example 1, cascade developer containing black toner was used. Subsequent to the development of the first color, the sheet surface was retained for 15 seconds in vapor of trichlorethylene to fix image and recharged.

A similar result to that of the Example 1 was obtained.

EXAMPLE 5

Instead of the second magenta color liquid developer in Example 1, a cyan color liquid developer dispersed with phthalocyanine blue was used.

A black and cyan color image was obtained upon the same procedures as those of Example 1.

The portion in red ink in the original was copied to be in cyan color.

EXAMPLE 6

In place of the first black liquid developer of Example 1, green liquid developer disposed with phthalocyanine blue and Benzidine Yellow GR, was used. The black image in the original was copied to be in pure black, and the portion in red ink was copied in magenta color.

EXAMPLE 7

The original used in Example 5 was replaced by a sheet of white art paper, on which descriptions were made in black and blue inks.

The description in black ink copied in bluish black color and that in blue was copied in cyan color.

What is claimed is:

1. An electrophotographic process which comprises uniformly charging a surface of a photoconductive insulating layer having light-sensitivity in an intrinsic sensitive region and extended spectrum region, said photoconductive insulating layer exhibiting light fatigue when exposed to light in the range of its intrinsic sensitive region, imagewise exposing the surface to light which covers the entire light-sensitive region of the light-sensitive layer from an original which includes a first colored portion which absorbs substantially all of said light and a second colored portion which absorbs

from said light substantially only the wavelength range corresponding to said intrinsic sensitive region to form on said photoconductive insulating layer an electrostatic latent image corresponding to said first colored portion and a substantially non-conductive area corresponding to said second colored portion, developing the electrostatic latent image by electroscopic developer, again uniformly charging the surface of the layer to form a second electrostatic latent image at least at said substantially non-conductive area and developing the said second electrostatic latent image with electroscopic developer.

2. An electrophotographic process as claimed in claim 1, wherein said photoconductive insulating layer comprises dye-sensitized zinc oxide dispersed in resinous binder.

3. An electrophotographic process as claimed in claim 2, wherein the ratio by weight of the zinc oxide to the resinous binder varies between 8 : 1 to 2.5 : 1.

4. An electrophotographic process as claimed in claim 1, wherein said photoconductive insulating layer comprises dye-sensitized titanium dioxide dispersed in resinous binder.

5. An electrophotographic process as claimed in claim 1, wherein the first and the second developments are carried out by a liquid development process.

6. An electrophotographic process as claimed in claim 1, wherein color of the electroscopic developer used in the second development step is different from that of the first development step.

7. An electrophotographic process as in claim 1 where said first colored portion of the original is black and said second colored portion is any color other than black.

8. An electrophotographic process as in claim 1 where said intrinsic sensitivity region corresponds to the ultraviolet wavelength range.

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