

July 23, 1974

YASUO TAMAI

3,825,421

PROCESS FOR FORMING AN IMAGE ON INSULATIVE MATERIALS

Filed Oct. 29, 1971

2 Sheets-Sheet 1

FIG. 1

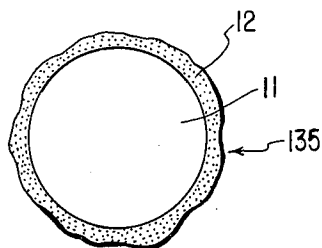


FIG. 2

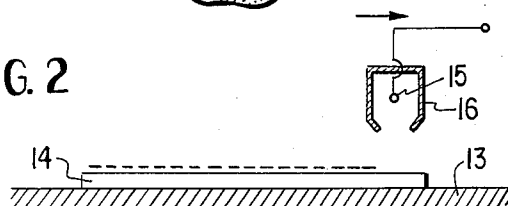


FIG. 3

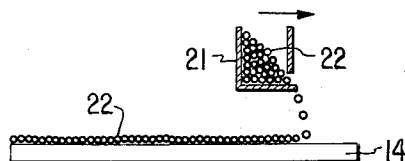
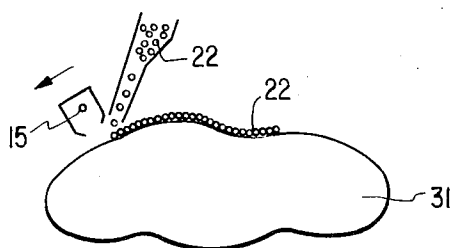


FIG. 4



July 23, 1974

YASUO TAMAI

3,825,421

PROCESS FOR FORMING AN IMAGE ON INSULATIVE MATERIALS

Filed Oct. 29, 1971

2 Sheets-Sheet 2

FIG. 5

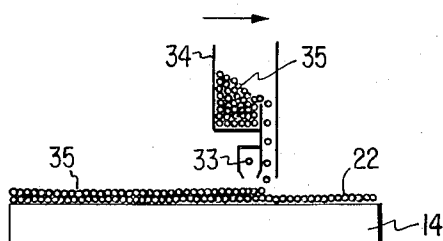


FIG. 6

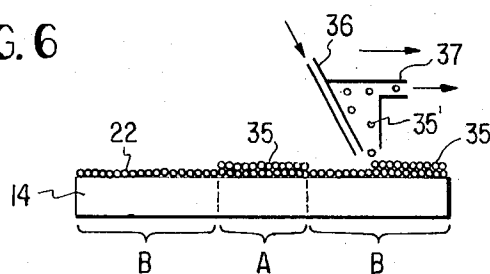


FIG. 7

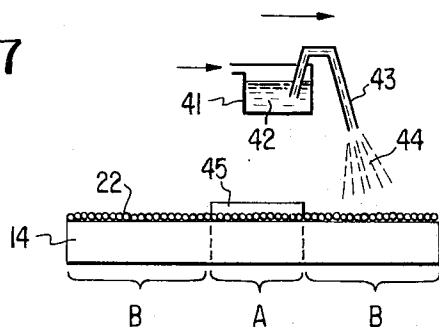
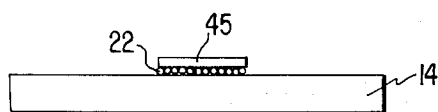


FIG. 8



1

2

3,825,421

PROCESS FOR FORMING AN IMAGE ON INSULATIVE MATERIALS

Yasuo Tamai, Asaka, Japan, assignor to Fuji Photo Film Co., Ltd., Kanagawa, Japan

Filed Oct. 29, 1971, Ser. No. 193,890

Claims priority, application Japan, Oct. 29, 1970, 45/95,488

Int. Cl. G03g 13/22

U.S. Cl. 96—1 R

14 Claims

ABSTRACT OF THE DISCLOSURE

A process for forming an image on an insulative material comprising the steps of:

dispersing electroconductive powder on at least one surface of said insulative material and electrostatically charging the same no later than said dispersing to thereby form a layer of said electroconductive powder on said insulative material;

dispersing photoconductive particles onto said layer of electroconductive powder and electrostatically charging the same no later than said dispersing to thereby form a layer of said photoconductive powder on said layer of electroconductive powder;

subjecting the thus formed layer of photoconductive particles to imagewise exposure of the original image; removing said photoconductive particles in the exposed areas; and

fixing the remaining photoconductive particles to thereby obtain an image on the surface of said insulative material.

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to an improvement in electrophotographic processes, and particularly relates to an improvement in an electrophotographic scribing or image formation process on an insulative material utilizing photoconductive particles as the photoconductive element therein.

Description of the Prior Art

One variation of standard electrophotographic processes recently proposed is a process utilizing a combination of a photoconductive powder containing a transparent core and an electroconductive plate (for example the process disclosed in Jap. Pat. Pub. 12,385/69). This electrophotographic process consists of the steps of first dispersing a photoconductive powder and then electrostatically charging the photoconductive powder, or else dispersing a previously charged photoconductive powder, followed by additional charging if desirable, on an electroconductive support material, subjecting the thus dispersed and charged powder to imagewise exposure of an original image, removing the powder of which the electrostatic charge is dissipated or decreased by exposure, and either fixing the remaining powder in situ or after transfer thereof. The photoconductive powder used consists of a photoconductive material and powder core material provided therein having an absorption coefficient not exceeding $1.3 \times 10^2 \text{ mm}^{-1}$ for the major part of the radiation in the sensitive wavelength region of the photoconductive material. This process is capable of reproducing clear, sharp images on electroconductive plates and is employed in electrophotographic platemaking apparatus for scribing onto steel plates etc.

The above-mentioned process, however, is incapable of reproducing images on insulative materials.

The present inventors have provided a novel imaging

process capable of obtaining images on the surface of insulative materials.

SUMMARY OF THE INVENTION

The present invention relates to an electrophotographic scribing process for insulative materials comprising the steps of:

either dispersing electroconductive powder on an insulative material simultaneously with electrostatic charging thereon or dispersing electroconductive powder on said insulative material which previously has been charged, thereby forming thereon a layer of said electroconductive powder;

dispersing a photoconductive powder on said layer followed by electrostatic charging thereon, or dispersing said photoconductive powder which has been previously charged onto said layer, followed eventually by additional charging if desired;

subjecting said dispersed photoconductive powder to imagewise exposure of an original image;

removing said photoconductive powder in the areas where the electrostatic charge thereon is dissipated or decreased by said exposure; and

fixing the remaining photoconductive powder.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross sectional view of an example of photoconductive particles employed in the process of the present invention;

FIGS. 2-8 are schematic side-views showing the steps of a scribing process for an insulative material according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The insulative material employed in the invention can be in any shape, e.g., a flat plate. It will be apparent to one skilled in the art that the exact shape of the insulative material does not form a part of the present invention.

The electroconductive powder to be dispersed on said insulative material can be a metal powder, metal spheres, a resin powder covered with metal, electroconductive carbon spheres, a resin powder covered with electroconductive carbon, glass spheres covered with an electroconductive tin oxide layer, cuprous iodide etc. In short, any powder, be it homogeneous or composite, which is capable of carrying an electric current without degradation may be used in the present invention. The electroconductive powder preferably has a diameter ranging from 5 microns to 2 millimeters.

The preferred electroconductive powders have a conductance greater than $1 \times 10^{-6} \text{ v. cm}^2$ specific surface conductance (the conductance determined when electrodes having 1 unit length are disposed in parallel having with a distance 1 unit between them) when the powders are laid on the insulating base. The most preferred specific surface conductance range is ca. 10^{-4} – 10^4 v. cm^2 , but it is to be understood such range is not mandatory.

In addition to those particles set out above, particles having a diameter of 50 to 500μ such as glass balls, siliceous sand, alumina, china and the like coated on their surface with a mixture of carbon black and a resin, or similar core material particles coated with highly conductive metals such as Ag, Ni, Cu and so on by chemical plating, are other examples of preferred electroconductive particles. The electroconductive particles are preferably charged, via the insulative material to 100 to 2,000 volts most preferably 200 to 1,000 volts.

Deposition of the electroconductive powder on the surface of said insulative material to form a layer thereon can be realized by dispersing the electroconductive pow-

der on the insulative material which has been previously charged, or by dispersing the electroconductive powder simultaneously with electrostatic charging.

It is, of course, necessary to disperse the powders to have good contact with each other. This depends on the particle size, however, it is, generally preferred to have a thickness, of three or four layers of closely packed particles. Thicker layers, of course, can be used. The minimum thickness generally used is about 20μ , as this insures an acceptable necessary specific surface conductance to provide good results.

The process according to this invention will now be further explained with reference to the attached drawings wherein:

FIG. 1 shows a cross section of one example of a photoconductive powder particle employed in this invention.

The photoconductive particle 35 is composed of a transparent core 11 and a photoconductive insulative layer 12 thereabout. The transparent core 11 preferably has an absorption coefficient not exceeding $1.3 \times 10^2 \text{ mm.}^{-1}$ for the major part of the radiation in the sensitive wavelength region of the photoconductive layer 12 (for best results a $\pm 50 \text{ m}\mu$ shift from the peak). To facilitate the fixing step it is most preferred that at least one of the core material 11 or the insulative photoconductive layer 12 contains a thermoplastic resin material or a material which is soluble in a suitable solvent which can be applied to achieve fixing.

Suitable solvents for fixing will, of course, depend on the material to be marked and the resinous material, if used, in the photoconductive powder; generally speaking, trichloroethylene, tetrachloroethylene, acetone, MEK, MIBK, ethyl acetate, propyl or butyl acetate, toluene, xylene are used.

Representative of preferred photoconductive particles for use in the present invention are those disclosed in British Pat. No. 1,165,017.

Usually the photoconductive particles will have a size of 10 to 200 microns, with a size of 20 to 80 microns being most preferred.

The thickness of the photoconductive particle layer is generally in accordance with such layers as are known to the art, and must be sufficient to permit the layer to perform its image-yielding function. Usually a thickness of at least two of the smaller sized photoconductive particles is required, and thus the preferred photoconductive layers have a thickness of 20 to 200 microns, though obviously thicker layers can be used. For instance, using particles of a specific gravity of 1.3 as disclosed in the above British patent a layer thickness of over 20 microns is used.

One skilled in the art will appreciate that it is necessary to charge such a photoconductive layer to a degree sufficient to enable image formation, and will be able to easily determine such charging values. A surface voltage of about 350 volts or greater is generally used.

Preferred thermoplastic resin materials include polymethylmethacrylate, polystyrene, poly α -methylstyrene, polyamide, polycarbonate, polyvinylchloride, polyvinylbutyral and the like, which are polymerized or condensed polymers having a secondary transition point higher than room temperature, e.g., in the range 80 to 200°C .

FIG. 2 shows the step of electrostatic charging on the surface of an insulative flat plate 14 on which the image is to be reproduced. The insulative plate 14 is placed on an electroconductive support plate 13 and exposed to corona discharge generated by corona electrode 15 provided in shield case 16 moving above the surface of plate 14. The corona electrode 15 is externally supplied with a high electric potential (a negative potential in this case). Electrostatic charging can also be carried out by other charging processes known to the art such as frictional charging. The exact charging method is not of great importance.

Electroconductive powder 22 is dispersed as shown in FIG. 3 onto the surface of thus charged insulative plate 14 from a reservoir 21 to form a uniform layer.

FIG. 4 shows the dispersion of electroconductive powder 22 on the surface of an insulative material of irregular shape. In this case the electroconductive powder 22 contained in a container provided with an appropriate outlet thereunder is made to fall onto the surface of the material 31 in a layer and is simultaneously exposed to a corona discharge generated by the corona electrode 15, thereby being deposited in a uniform layer on the surface thus charged.

FIG. 5 shows the step of dispersing photoconductive particles 35 on the insulative material 14 which already is provided with a layer of electroconductive powder 22 by means of the step explained in FIG. 4. The photoconductive particles 35 supplied from the container 34 are electrostatically charged by means of corona discharge electrode 33 and dispersed on the layer of electroconductive powder 22. Uniform dispersion of said photoconductive particles can be accomplished, for example, by the dispersing device disclosed in Jap. Pat. Pub. 8,838/70 in which the powder is dispersed as solid-gas sol. It is naturally also possible to apply electrostatic charging to said particles after dispersion thereof.

FIG. 6 shows the step of development with air jet after imagewise exposure thereon.

The photoconductive particles 35 in the exposed area B lose their electrostatic charge and are eliminated by the air jet supplied by duct 36 displaced in the direction of arrow. 35' indicates the photoconductive particles thus removed by the air jet and collected in a duct 37 of reduced pressure.

In this case the electroconductive powder 22 electrostatically deposited on the insulative material 14 is not removed therefrom by the air jet, and the photoconductive particles 35 in the unexposed area A remain on the layer of electroconductive powder as these particles still retain electrostatic charge. The air jet supplied from the duct 36 is regulated so as to not remove the photoconductive particles in the unexposed area.

It is important that the electroconductive powder 22 be firmly retained on the insulative material 14, since the separation of this powder from the recovered photoconductive particles 35' at the cycled use thereof. For this purpose the insulative material 14 is required to be highly insulative, and preferably has a resistivity of about 10^{11} ohm.cm or higher most preferably 10^{13} ohm.cm or higher. At lower resistivity, the conductive powder cannot be retained stably on the surface of insulative material 14 and is apt to contaminate the recovered photoconductive particles. To allow for the case where such might happen, it is preferred to have a difference in specific gravity or magnetic properties between the electroconductive powder and the photoconductive particles to facilitate the separation thereof.

FIG. 7 shows the step of fixing the image consisting of the photoconductive particles by means of a fixing head displaced in the direction of the arrow after the above-mentioned steps. A solvent 42 contained in the container 41 is sprayed in mist form 44 from a nozzle 43. The component soluble in the solvent (the resinous component in most cases) in the photoconductive particles is dissolved and firmly sticks onto the surface of insulative material 14 together with the photoconductive particles in the unexposed area A to form the fixed image 45. If the electroconductive powder 22 is composed of a material insoluble in the solvent, such as a metal, the electroconductive powder is not dissolved by the sprayed solvent and therefore is not fixed onto the insulative material 14 when said solvent is evaporated. Thus, if the electroconductive powder 22 is desired not to be fixed onto the surface of the insulative material 14 in the non-image area B thereof, the solvent 42 is preferably one which does not dissolve

the insulative material 14 or the electroconductive powder 22.

The electroconductive powder 22 sticking to the non-image area B can be removed by exposing the assembly to a corona discharge of inverted polarity with respect to that employed in the step shown in FIG. 2 or of an alternating polarity, to thereby eliminate the electrostatic charge remaining thereon. An air jet may then be used to remove the powder 22 at area B. Mechanical elimination of the charge and removal by means, for example, of a brush are among alternative removal procedures.

Charge elimination can also be achieved by the presence of a small amount of non-film-forming antistatic agent in the solvent 42 employed in the step of FIG. 7, or by passing the insulative material through grounded electroconductive particles as explained in Jap. Pat. Pub. 3,669/69.

FIG. 8 shows the image 45 containing the electroconductive powder 22 thus formed on the insulative material 14 according to the process of this invention thus far explained. Thus this invention enables one to electrophotographically obtain an image on the surface of an insulative material.

The process of this invention is applicable to insulative materials and materials provided with an insulative surface, such as a metal plate provided thereon with a resinous layer, a metal plate provided thereon with an enameled layer, moulded plastics, plastic sheets, glass plates, glass blocks, glass bottles, etc.

The above material represents a sufficient disclosure to completely enable one skilled in the art to practice the invention. The following Examples are merely offered to show two typical processings in accordance with the present invention.

Example I

On an electrostatically charged polyethylene terephthalate film, a finely divided black powder comprising 10 parts of carbon black and 10 parts of phenol resin, having a mean particle diameter of about 50μ was cascaded. The charging of the film was carried out by a negative corona. The black conductive powder uniformly adhered on the film surface. The weight of the powder layer was 25 g./m.^2 – 30 g./m.^2 , and the layer showed a surface resistance of about $10^{-5} \text{ cm./square}$. On this black layer there was again spread a photoconductive powder which had been prepared according to the method described in Example I in British Patent 1,165,017. The coated weight of this second layer was about 85 – 110 g./m.^2 . The covered film was subjected to a negative corona with its carbon layer connected to ground. The initial potential of the top was -400 volts. An optically positive image was projected and the film was subjected to an air stream. Whereby the photoconductive powder remained only at the non-irradiated area giving a white image against a dark background.

Fixing of the image was carried out by spraying cyclohexane onto the film whereby the conductive powder did not dissolve at all. Then after the evaporation of the solvent, the conductive powder at the background area was eliminated.

Example II

A piece of glass plate was covered with silver coated small glass beads having a diameter of about 50μ with silver chemically plated thereon. The coated weight of the beads was 40 g./m.^2 . On this coating there was applied the photoconductive powder described in Example VIII in the above cited British patent. The coating weight was about 150 g./m.^2 . When this sheet was exposed to a negative corona an initial surface potential of about 500 volts was obtained. Then an air stream was carefully applied onto the plate to glow off only the photoconduc-

tive powder at the irradiated portion. The photoconductive powder image was then fixed by spraying trichloroethylene thereon. After the evaporation of the solvent, the conductive powder was removed by brushing.

What is claimed is:

1. A process for forming an image on an insulative material comprising the steps of:

dispersing electroconductive powder on at least one surface of said insulative material and applying electrostatic charge to the powder no later than said dispersing to thereby firmly retain but not physically bind said electroconductive powder on said insulative material;

dispersing photoconductive particles onto said layer of electroconductive powder and electrostatically charging the photoconductive particles to thereby form a layer of said photoconductive powder on said layer of electroconductive powder;

subjecting the thus formed layer of photoconductive particles to imagewise exposure of the original image; removing said photoconductive particles in the exposed areas; and

fixing the remaining photoconductive particles to thereby obtain an image on the surface of said insulative material.

2. The process of claim 1 wherein said insulative material has a resistivity of at least about 10^{11} ohm.cm.

3. The process of claim 1 wherein said electroconductive powder dispersed on said insulative material layer has a specific surface conductance of greater than about $1 \times 10^{-6} \text{ v. cm.}^2$

4. The process of claim 1 wherein said photoconductive particles comprise a photoconductive insulative layer about a transparent core having an absorption coefficient no greater than $1.3 \times 10^2 \text{ mm.}^{-1}$ for the major portion of the sensitive wave length region of the insulative layer.

5. The process of claim 4 wherein at least one of said core or said insulative layer contains a thermoplastic resin.

6. The process of claim 1 where the first charging is prior to dispersing the electroconductive powder.

7. The process of claim 1 where the first charging is simultaneously with dispersing the electroconductive powder.

8. The process of claim 1 where the second charging is subsequent to dispersing the photoconductive powder.

9. The process of claim 1 where the second charging is prior to dispersing the photoconductive powder.

10. The process of claim 9 where the second charging is prior to dispersing the photoconductive powder, and after said dispersing said electroconductive powder is additionally charged.

11. The process of claim 1 where the second charging is simultaneously with dispersing the photoconductive powder.

12. The process of claim 1 wherein said electroconductive particles are dispersed in a layer at least about 20 microns thick, and said photoconductive particles are dispersed in a layer at least about 20 microns thick.

13. The process of claim 1 wherein said photoconductive particles are charged to a surface voltage of at least about 350 volts.

14. A process for forming an image on an insulative material having a resistivity of at least 10^{11} ohm.cm. comprising the steps of:

forming a conducting layer of an electroconductive powder on one surface of said insulative material, said conducting layer having a specific surface conductance greater than $1 \times 10^{-6} \text{ v. cm.}^2$ and being formed of particles of a size of from 5 microns to 2 millimeters at least three layers deep;

at a point no later than the forming of the conducting layer, applying electrostatic charge to the conducting layer to firmly retain but not physically bind the layer on said insulative material;

7

forming a layer of photoconductive particles of a thickness of 10 to 200 microns on the thin formed and charged conducting layer, said layer of photoconductive particles having a thickness of at least 20 microns;
 electrostatically charging said layer of photoconductive particles to a surface voltage of greater than 350 volts at a point no later than subjecting the layer of photoconductive particles to imagewise exposure;
 imagewise exposing the thin charged layer of photoconductive particles to an original image;
 removing the photoconductive particles in the exposed areas; and
 fixing the remaining photoconductive particles to thereby obtain an image on the surface of said insulative material.

5

10

15

8

References Cited

UNITED STATES PATENTS

2,924,519 2/1960 Bertelsen ----- 96-1 R

FOREIGN PATENTS

1,165,017 9/1969 Great Britain ----- 96-1 R
 1,082,912 9/1967 Great Britain ----- 96-1 R
 990,538 4/1965 Great Britain ----- 96-1 R
 38/22,645 1963 Japan ----- 96-1 R
 234,016 8/1959 Australia ----- 96-1 R
 1,008,633 11/1965 Great Britain ----- 96-1.5

CHARLES E. VAN HORN, Primary Examiner

U.S. Cl. X.R.

96-1.5; 117-201, 215, 17.5, 37 R