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E. C. GIAIMO, JR
ELECTROSTATIC PRINTING

2,990,280

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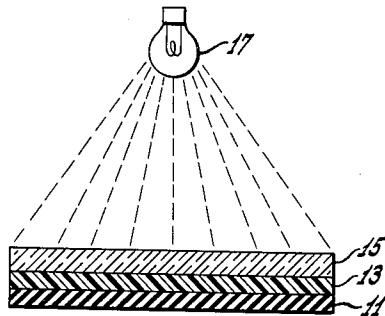


Fig. 1.

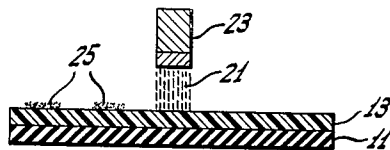


Fig. 2.

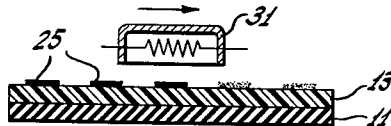


Fig. 3.

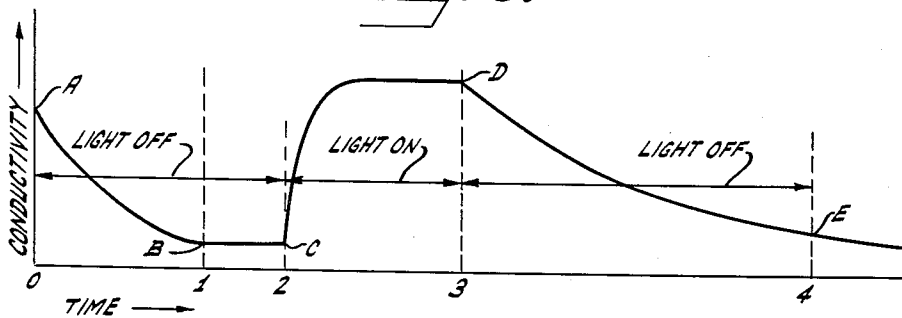


Fig. 4.

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ELECTROSTATIC PRINTING

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This invention relates to electrostatic printing and more particularly to improved methods and means for producing visible powder images in substantial configuration with a latent conductivity pattern in a photoconducting layer.

Methods of electrostatic printing are known wherein a latent conductivity pattern is produced in a dark adapted photoconducting layer by momentarily projecting a light image incident upon the layer. During the decay of the conductivity pattern so produced, it is developed to produce a visible image. Development is generally accomplished by one of three methods. In the first method, the photoconducting layer is electrostatically charged by ion bombardment utilizing a corona discharge apparatus. During bombardment electrostatic charges build up in the less conducting areas of the photoconducting layer to produce a latent electrostatic image. The latent electrostatic image is then developed to a visible image by applying an electroscopic powder to the photoconducting layer. In the second method of development, a uni-directional electric field is established through the photoconducting layer and, with the electric field applied, a dry physical mixture of electrostatically attractable developer powder particles and carrier particles is contacted across the surface of the photoconducting layer. Developer powder particles deposit in those areas which have not been exposed to light to produce a visible powder image. In the third method of development, an electrolyte including complex silver salts in solution is contacted to the photoconductive layer and at the same time a potential difference is established between the electrolyte and a conducting backing member underlying the photoconducting layer. Silver ions are attracted to the conductive areas of the photoconducting layer where each silver ion gains an electron and deposits on the layer as a silver atom to produce a visible image.

All of the foregoing development methods have some disadvantages. In the first method, a corona discharge is employed requiring potentials of the order of 7,000 volts. In the second, potentials ranging from 500 to 1500 volts are preferred, optimum results being obtained with potentials ranging from 700 to 1500 volts. In the third method, lower potentials of the order of 25 to 150 volts are employed, however, considerable current, of the order of 1/2 an ampere per square centimeter, is drawn from the power supply during development. The high voltages required in the first two methods require special power supply apparatus. The current requirement of the third method results in appreciable power consumption. The second and third methods require accurate control of developing potentials to prevent arcing through the photoconducting layer. And, in addition to these disadvantages, the third method is only capable of producing a visible image which is a negative of the original light image employed.

Accordingly, it is a general object of this invention to provide improved methods of electrostatic printing.

Another object is to provide improved methods for converting a latent conductivity pattern into a visible powder image which methods obviate any need for externally applied electric fields.

Yet another object is to provide improved methods of electrostatic printing wherein a visible powder image is produced on a photoconducting layer, said visible image

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being either a negative or a positive of an original light image projected onto the layer.

In general, the foregoing objects and other advantages are attained in accordance with this invention which includes the following steps. First, a dark adapted recording element which includes a photoconducting insulating material is exposed to a radiant image to produce in the photoconducting material a latent conductivity pattern. Within the decay time of the conductivity pattern so produced, a mixture of a carrier material and developer powder particles is contacted across one surface of the recording element. It is essential that the carrier material and the developer powder particles, employed in the mixture, be separated, one from the other, in the triboelectric series. When a mixture is used in which the developer powder particles are triboelectrically positive with respect to the carrier material, developer powder deposits in the less conducting areas of the recording element. Conversely, when the developer powder particles are triboelectrically negative with respect to the carrier material, they deposit in the more conducting areas of the recording element.

Thus, in accordance with this invention a visible powder image is produced by the attraction of developer powder particles to a photoconducting recording element solely as a result of the triboelectric relationship existing between the carrier particles and the developer powder particles in the mixture and as a result of the triboelectric charges generated during the contacting of the mixture with the photoconducting surface.

The foregoing objects and other advantages will be more fully described in the following detailed description when read in connection with the accompanying drawings in which:

FIGURE 1 is a partially sectional, partially schematic view of an apparatus for producing a latent conductivity pattern in a photoconducting layer.

FIGURE 2 is a partially sectional, partially schematic view of one means for producing a powder image from the latent conductivity pattern of FIGURE 1.

FIGURE 3 is a partially sectional, partially schematic view of an apparatus for fixing the developed image produced in FIGURE 3.

FIGURE 4 is a curve illustrating changes in the conductivity pattern of an incremental area of a photoconducting layer when processed in accordance with this invention.

Similar reference characters are applied to similar elements throughout the drawings.

Referring to FIGURE 1, a photoconducting layer 13, such as photoconducting zinc oxide dispersed in resinous polysiloxane and supported on a backing 11, such as paper, is dark adapted prior to the time when it is desired to use it as a recording element. Dark adaption is defined herein and in the appended claims to mean that the photoconducting layer 13 is conditioned, prior to exposure, by one of the following methods: (1) the photoconducting layer 13 is stored in darkness at room temperature for at least one hour, preferably about 24 hours, (2) the photoconducting layer is heated by resistance elements, in an oven, or by infrared radiation until it reaches a temperature of from about 30° C. to 180° C. in darkness, and (3) method (1) in combination with method (2).

A photographic transparency 15, bearing an image to be copied, is positioned on top of the dark-adapted photoconducting layer 13. An exposure is then made using a light source 17, such as a 100 watt tungsten lamp spaced about 24 inches from the photographic transparency 15, for about one second. A light image is thus projected on to the photoconducting layer 13 causing an increase in the electrical conductivity of the illuminated areas.

Other photographic exposure methods, such as by projection of an image, are equally applicable. This change in conductivity over portions of the photoconducting layer 13, is referred to as a conductivity pattern. The conductivity pattern is latent and is in substantially the same configuration as the incident light image.

The photographic transparency is then removed from the photoconducting coating and the latent conductivity pattern developed into a visible image by applying thereto a developer powder substance. This may be accomplished, as illustrated in FIGURE 2, by passing a developer brush 21 containing developer powder particles across the photoconducting layer 13. The developer brush 21 comprises a mixture of magnetic carrier particles, for example powdered iron, and about 1 to 6% developer powder particles. The mixture is secured in a magnetic field by a magnet 23 to form the developer brush 21. When developer powder particles are selected which are triboelectrically positive with respect to the magnetic carrier particles, they will be triboelectrically attracted to and held on those areas 25 of the photoconducting layer which have not been struck by light and which, therefore, have a higher resistivity than light struck areas.

Methods of development may be employed other than that described in connection with FIGURE 2. For example, a mixture of carrier particles, such as glass beads, and developer powder particles may be cascaded across the photoconducting layer. For a more detailed description of cascade and magnetic brush development reference is made to "Electrofax-Direct Electrophotographic Printing on Paper," by C. J. Young and H. G. Greig, RCA Review, volume 15, No. 4.

For use in any of the foregoing methods of development, a preferred developer powder may be prepared as follows: A mixture comprising 200 grams of 200 mesh Piccolastic resin 4358 (an elastic thermoplastic resin composed of polymers of styrene, substituted styrene and its homologs) marketed by the Pennsylvania Industrial Chemical Corporation, Clairton, Pennsylvania, 12 grams of Carbon Black G, marketed by the Eimer and Amend Company, New York, New York, 12 grams of spirit Nigrosine S.S.B., marketed by the Allied Chemical and Dye Company, New York, New York and 8 grams of Iosol Black, also marketed by the Allied Chemical and Dye Company, are thoroughly mixed in a stainless steel beaker at about 200° C. This mixing and heating should be done in as short a time as possible. The melt is poured into a brass tray and allowed to cool and harden. The hardened mix is then broken up and ball-milled for about 20 hours. The powder is then screened through a 200 mesh screen and is then ready for use as a developer powder. This powder takes on a positive electrostatic charge when mixed with glass beads, or iron filings. It therefore develops a visible image in those areas on the photoconductive layer which have not been struck by light i.e. the less conductive areas of the photoconductive layer.

Good contrast in the visible image may be obtained employing the above described developer powder in the magnetic brush method of development. This is accomplished by mixing about 100 grams of the developer powder with about 30 grams of fine iron powder and ball-milling the mix for about 4 more hours. A magnetic brush containing developer powder prepared in this manner tends to leave less spurious deposit of the powder in the background areas of the developed image.

Developer powders may be chosen from a large class of materials, for example: "Vinsol resin" a thermoplastic resin derived from pine wood, and containing phenol, aldehyde and ether groups, produced by the Hercules Powder Company, Wilmington, Delaware, and the xerographic developer powders described in U.S. Patent 2,753,308 to Richard B. Landrigan, sulfur, carbon, gum

opal, gum sandarac, nylon, polystyrene, sealing wax and other natural or synthetic resins or mixtures thereof. The developer powder particles may be coated with a thin layer of material for the purpose of modifying the chemical, physical or electrical properties thereof.

A preferred carrier material for use in a magnetic brush consists of "alcoholized iron," that is, iron particles free from grease and other alcohol-soluble impurities. These iron particles are preferably relatively large in size as compared with the developer powder particles, being in their largest dimension about .002" to .008". Satisfactory results are also obtained using a carrier consisting of a somewhat wider range of sizes from about .001" to about .020". Materials such as steel, alloys of aluminum, nickel and cobalt and other magnetic materials may be used. These carrier particles may be employed in the cascade method of development as well as in the magnetic brush method.

In the cascade method of development many carrier materials other than the iron described above are suitable. Some of these include glass beads, brass copper and other metallic particles as well as various resins or resin coated materials as described in U.S. Patent 2,753,308 op. cit. Preferably these carrier materials comprise spherical particles in the order of 20 to 30 mesh. A carrier to developer powder ratio of about 100 to 1 is preferred although this ratio may vary as widely as between 250 to 1 and 25 to 1 depending on the particular components selected.

In either the magnetic brush or the cascade method of development it has been found that improved results are obtained when a carrier material is employed which is more conductive than the material of the developer powder particles.

By proper selection of a carrier material and a developer powder either positive or negative images may be selectively produced from an original. For example, when the developer mix comprises a carrier material of iron or glass beads and a developer powder such as "Vinsol resin" or sulfur, developer powder particles will be deposited in the more conducting areas on the photoconducting areas on the photoconducting layer 13 to produce a negative of an original image.

Ordinarily, once a visible powder image has been produced on the photoconducting layer 13, the image will be fixed thereon by some suitable means. A preferred means for fixing a thermoplastic developer powder image is illustrated in FIGURE 3. A resistance heating unit 31 is passed over the image-bearing photoconducting layer 13. When a temperature above the melting point of the thermoplastic developer powder is applied thereto, the powder melts and, upon cooling, becomes bonded to the photoconducting layer. Other means are available for fixing the developed image. For example, the image may be fused in an oven or the heating element 31 may comprise an infrared lamp. Fixing may also be accomplished with a fixative spray such as varnish, shellac or polymethyl-methacrylate resin as are commonly employed for the fixing of charcoal drawings.

Other photoconducting layers usable in electrophotography may be employed in the methods of this invention. Some of these are described by C. J. Young and H. G. Greig op. cit. A preferred composition may be prepared by intimately mixing 100 grams of a photoconducting white zinc oxide with 65 grams of a 60% solution of resinous polysiloxane in xylene and 85 grams of toluene. After ball-milling to obtain a smooth consistency, the mixture is coated on the surface of a proper backing member and dried. Any standard coating technique may be used, such as flowing, spraying, dipping, spin coating, or brushing on. Suitable backing members include paper, mica, glass or various cellulosic insulating sheets. In addition to these, relatively conducting backing members may also be employed, however, it is pre-

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ferred to use an insulator having a volume resistivity of 10^{12} ohm-cms. or higher.

An essential part of the developing procedure is that it must be carried out during the decay of the conductivity pattern in the photoconducting layer. Referring to FIGURE 4, there is shown a plot of conductivity in an incremental area of the photoconducting layer with respect to time. The photoconducting layer is dark adapted for a period 0-1, as described heretofore, until its conductivity is reduced from a value such as shown at A to a steady state of minimum conductivity as shown by B-C. Light is turned on during the period 2-3 which is the period of exposure to the light image. During this time the conductivity rises to a maximum value as shown by the curve C-D. After the light is turned off at 3, the conductivity begins to fall to a minimum value during the period 3-4 as shown by the curve D-E. It is during the interval 3-4 that development of the latent conductivity pattern must take place. Development is preferably carried out as soon as possible in order to take advantage of larger differences in conductivity. In this regard, it is generally best to select a photoconducting layer having a conductivity decay period 3-4 of at least 10 seconds. A photoconducting layer such as photoconducting white zinc oxide dispersed in resinous polysiloxane has a very long period of decay and development may take place during a period of an hour or more after exposure to light. However, development preferably takes place as soon as possible after exposure to the light image.

The phenomena on which operativeness of this invention is based are not well understood. However, it is believed that the following theory of operation is a possible explanation and will be helpful toward an understanding of the invention. When a developer powder is mixed with a carrier material it takes on a triboelectric charge the polarity of which depends on the relative position of the two materials in the triboelectric series. Thus, if the developer powder is above the carrier material in the series it will take on a positive charge i.e. it will give up a negative charge (electrons) to the carrier material. When the mixture is contacted across a latent conductivity pattern, some of the electrons previously acquired by the carrier material are injected into the surface. Since the shallow traps in the unexposed areas are mostly empty, a sufficient number of electrons injected into the unexposed areas by the carrier material fall into these traps and remain therein for a time sufficient to be felt by the triboelectrically positive developer powder thereby causing the powder to be attracted thereto and electrostatically held on the surface. In the more conductive (exposed) areas on the photoconductive layer the shallow traps are largely filled by the previous light exposure and electrons injected in the surface by the carrier material do not become trapped but rather appear capable of moving into and out of the photoconductive layer with equal facility. Thus electrons injected into the conductive areas by the carrier material do not remain therein beyond the time during which the carrier material is in contact with such areas. In this way the attractive force between carrier material and developer powder remains substantially constant while passing over conductive areas and no powder is deposited thereon.

If the developer powder is below the carrier material in the triboelectric series it takes on a negative charge i.e. electrons are transferred from the carrier material to the developer powder. When the mixture is contacted across a conductive area of a photoconductive layer, electrons, produced by the light exposure, are withdrawn by the carrier material making it essentially neutral and in effect transferring a net positive charge from the carrier to such areas. This positive charge is felt by the negative developer powder and, since the powder is no

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longer strongly attracted to the carrier material, it is attracted to and adheres in the conductive areas. When the mixture passes over a non-conductive area, essentially all electrons contained therein are deeply trapped and hence cannot be withdrawn therefrom by the carrier material. As a result, the carrier material retains its triboelectric attraction for the developer powder and no deposition takes place in non-conductive areas.

What is claimed is:

1. A method of producing a visible powder image on a dark adapted uncharged electrophotographic element comprising a substrate having a coating thereon and in intimate contact therewith of a finely-divided photoconductor dispersed in an electrically insulating vehicle; said method comprising the steps of: maintaining said element in darkness and, without applying any electric field to said element, exposing said coating to a light image to produce therein a latent conductivity pattern in substantial configuration with said light image, then, in the absence of any electric field externally applied through said element, contacting a surface of said element with a mixture of a carrier material and developer powder particles separated from said carrier material in the triboelectric series, said developer powder particles being attracted to said surface solely as the result of the triboelectric relationship existing between said carrier material and said developer powder particles in said mixture and the triboelectric charges generated during the contacting of said mixture with said surface.

2. A method of producing a visible powder image on a dark adapted uncharged electrophotographic element comprising a substrate having a coating thereon and in intimate contact therewith of a finely-divided photoconductor dispersed in an electrically insulating vehicle; said method comprising the steps of: dark adapting said element to substantially reduce the conductivity of said coating, maintaining said element in darkness and, without applying any electric field to said element, exposing said coating to a light image to produce therein a latent conductivity pattern in substantial configuration with said light image, then, in the absence of any electric field externally applied through said element, contacting a surface of said element with a mixture of a carrier material and developer powder particles separated from said carrier material in the triboelectric series, said developer powder particles being attracted to said surface solely as the result of the triboelectric relationship existing between said carrier material and said developer powder particles in said mixture and the triboelectric charges generated during the contacting of said mixture with said surface.

3. The method of claim 2 wherein said step of dark adapting said element is accomplished by storing said element in darkness for at least one hour prior to said exposing step.

4. The method of claim 2 wherein said step of dark adapting said element is accomplished by heating said element in darkness to a temperature of at least 30 degrees centigrade prior to said exposing step.

5. The method of claim 2 wherein said developer powder particles are triboelectrically positive with respect to said carrier material and the visible image produced therewith is a positive reproduction of said light image.

6. The method of claim 2 wherein said developer powder particles are triboelectrically negative with respect to said carrier material and the visible image produced therewith is a negative reproduction of said light image.

7. The method of claim 2 wherein said carrier material comprises magnetic particles.

8. The method of claim 2 wherein said carrier material comprises glass beads.

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