

Oct. 18, 1960

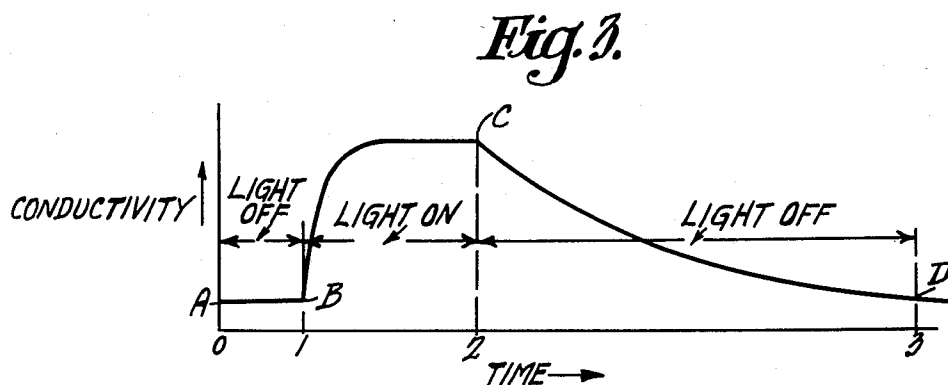
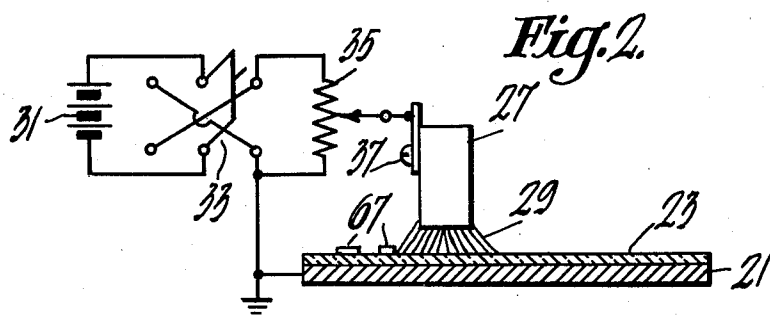
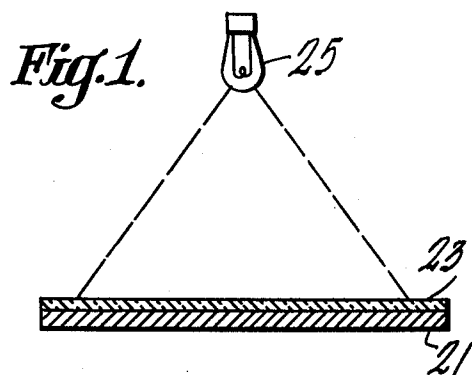
E. C. GIAIMO, JR

2,956,874

PHOTOCONDUCTIVE PHOTOGRAPHY

Filed May 1, 1956

2 Sheets-Sheet 1



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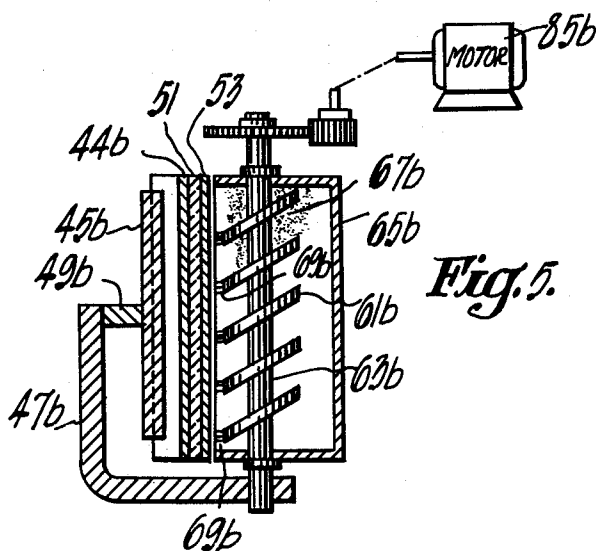
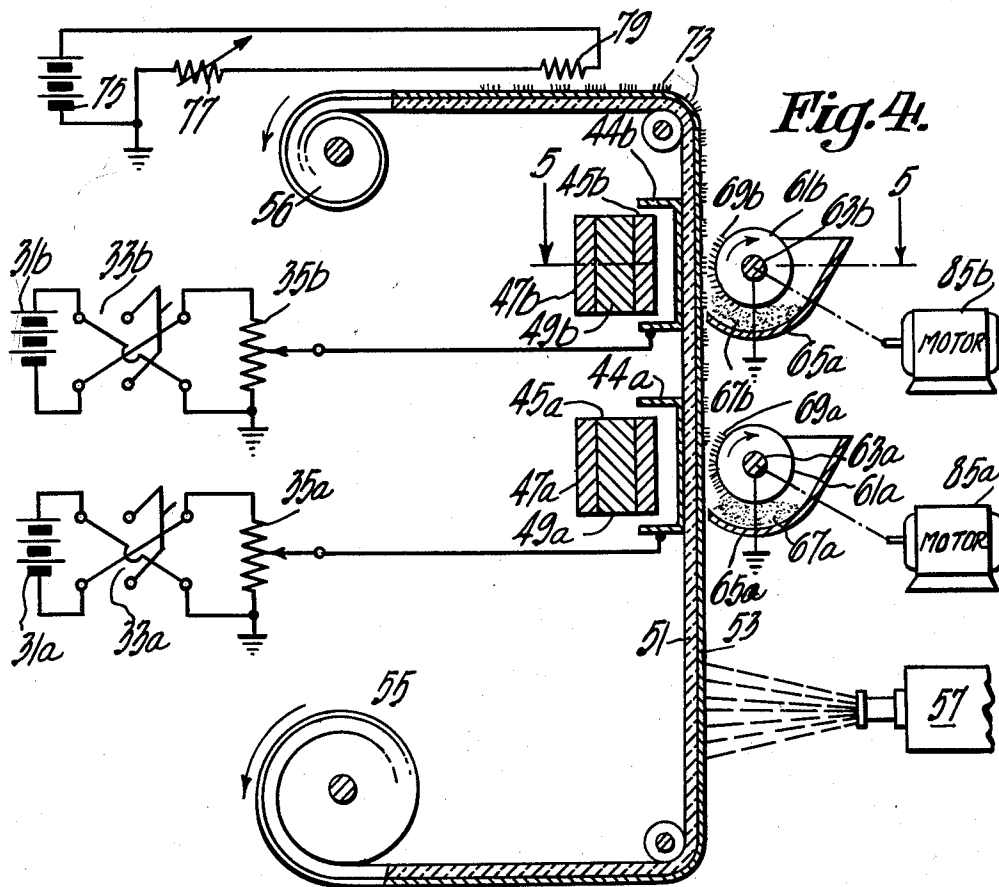
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PHOTOCONDUCTIVE PHOTOGRAPHY

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2 Sheets-Sheet 2



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1

2,956,874

PHOTOCONDUCTIVE PHOTOGRAPHY

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7 Claims. (Cl. 96—1)

This invention relates to photoconductive photography and particularly, but not necessarily exclusively, to improved photoconducting methods and means for producing visible powder images in substantial configuration with a latent conductivity pattern in a photoconducting layer.

In one type of photoconductive photography process, a photoconducting layer is first electrostatically charged by bombardment by charged particles as by the discharge from a corona discharge apparatus. Then, the charged surface of the photoconducting layer is exposed to a light image incident thereon, discharging the portions irradiated by the light rays, while leaving the remainder of the surface in a charged condition, thereby forming a latent electrostatic image substantially corresponding to the light image. The latent electrostatic image is developed to a visible powder image by applying thereto a developer powder which is held electrostatically to selected areas of the surface. The visible powder image thus formed may be fixed directly to the photoconducting surface or it may be transferred to another surface upon which the visible powder image may be desired and then fixed thereon.

In another type of photoconductive photography process, a light image is projected incident upon an uncharged photoconducting insulating layer producing therein a latent conductivity pattern. During the decay of the conductivity pattern, the photoconducting layer is electrostatically charged by bombardment by charged particles as by the discharge from a corona discharge apparatus. Electrostatic charges build up in the less conducting areas of the photoconducting layer thereby producing a latent electrostatic image in substantial configuration with the conductivity pattern. The latent electrostatic image is then developed to a visible powder image by any of the well-known methods, as by contacting the photoconducting insulating layer with an electroscopic powder.

Each of these processes requires a separate step of electrostatically charging the photoconducting layer by bombardment with charged particles either before or after the step of exposure to an incident light image. Other proposed processes have similarly included separate charging steps by other means. In addition, each of the foregoing processes requires the formation of a latent electrostatic image which must be stored for a finite period of time until the development of the image is effected.

An object of the invention is to provide improved methods and means of photoconductive photography.

Another object is to provide improved photoconducting methods and means for producing a powder image in substantial configuration with a latent conductivity pattern, which improved methods omit the step of electrostatically charging the photoconducting layer.

Another object is to provide improved methods and means for direct conversion of a latent conductivity pattern into a visible powder image.

In general, the processes of the invention include establishing a latent conductivity pattern in a photoconduct-

2

ing layer. Such pattern may be established by storing the photoconducting layer in darkness and then projecting a light image incident upon the photoconducting layer. Then, during the decay of the conductivity pattern, establishing a unidirectional electric field through the photoconducting layer and, with the electric field applied, contacting across the surface of the photoconducting layer a dry physical mixture of electrostatically-attractable developer particles and magnetic carrier particles separated from the developer particles in the triboelectric series. Developer particles deposit upon the photoconducting layer in substantial configuration with the conductivity pattern. The electric field is preferably high at the beginning and low at the end of the step of applying the developer particles. If desired, the contrast of the developed image may be varied; the developed image may be reversed; and the spurious deposit of developer powder particles in the background of the developed image may be controlled by varying the strength and direction of the electric field.

The foregoing objects and other advantages will be more fully described in the following detailed description when read in conjunction 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 an apparatus for producing a powder image from the latent conductivity pattern of Figure 1 according to the invention,

Figure 3 is a curve illustrating the conductivity of an incremental area of a photoconducting layer of Figures 1 and 2 during the steps of the invention,

Figure 4 is a partially sectional, partially schematic view of an apparatus for producing visible powder images from projected light images through the intermediate step of producing latent conductivity patterns according to the invention; and

Figure 5 is a sectional view along section lines 5—5 of Figure 4.

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

Example.—Referring to Figure 1, a photoconducting layer 23, such as photoconducting zinc oxide dispersed in a silicone resin, and supported upon a backing 21, such as aluminum, is maintained in darkness for several hours. An image of light within the range of spectral sensitivity of the photoconducting layer 23 incident upon the photoconducting layer 23 causing an increase in the electrical conductivity of the illuminated areas thereof. This change in conductivity over portions of the photoconducting layer is referred to as a conductivity pattern. The conductivity pattern is latent and is substantially in the same configuration as the incident light image. As shown in Figure 1, a photographic transparency (positive) 24 is placed upon the photoconducting layer 23 and exposed to light from a 40 watt tungsten source spaced about 20 inches from the photo conducting layer 23 for about one second.

Referring to Figure 2, the latent conductivity pattern is developed to a visible powder image by immediately contacting a developer brush across the surface of the photoconducting layer 23 with the backing 21 grounded. The developer brush comprises a magnetic pole piece 27, a mass of developer mix 29 including a physical mixture of magnetically-responsive carrier particles and developer powder particles held together and to the pole piece 27 by magnetic attraction, and connection means for a source of biasing voltage attached to the pole piece 27.

The magnetic pole piece 27 comprises an iron bar with a permanently magnetized pole at one end thereof.

The magnetic pole produces an external magnetic field which attracts and holds the mass of developer mix 29. The attracted mass of developer mix is loosely held and easily deformable to the contours of a surface with which it may be in contact. At the other end of the iron bar, a threaded hole and screw provides a connection means 37 for a source of biasing voltage to the developer brush.

A battery 31 or other source of biasing voltage is connected to the magnet 27 through the connection means 37, a double-pole, double-throw reversing switch 33 and a potentiometer 35. Thus, the applied biasing voltage may be changed in polarity and varied in magnitude.

The switch 33 and the potentiometer 35 are adjusted such that about +700 volts with respect to ground is applied to the magnet 27, and the developer mix 29 of the brush is contacted across the surface of the layer 23. During the period of contact, a unidirectional electric field appears between the mass of developer mix 29 and the backing 21 due to the biasing voltage applied between the brush and the backing 21. Developer powder particles 67 from the mass of developer mix 29 deposit on the less conducting areas of the photoconducting layer 23 producing a direct visible powder image thereon.

The visible powder image produced by the above-described procedure has a very high contrast characteristic and a minimum amount of spurious deposit in the background areas. This set of characteristics is considered ideal for line drawings and line prints. By reducing the biasing voltage and therefore the unidirectional field, the contrast between the dark and light areas of the image is reduced, making it possible to obtain any desired contrast characteristic over a very wide range of contrast values. A preferred range of positive voltage is about +500 to +1500 volts. Often, a moderate amount of developer powder deposits spuriously in the background areas of the visible powder image. Such spurious deposit may be reduced to a minimum value by adjusting the bias on the magnetic brush.

If the switch 33 is reversed and an increasing voltage applied to the magnet 27, a value is reached where there is developed a reverse visible powder image; that is, the powder deposits in the more conducting areas of the photoconducting layer. The contrast of the reverse visible powder image increases and the amount of spurious deposit in the background areas of the reverse image decreases as the negative voltage is increased in magnitude. A preferred range of negative voltage is about -500 to -1500 volts.

According to the invention, a direct or reverse visible powder image may be obtained from the same latent conductivity pattern. A direct visible powder image is a developed image wherein the developed areas correspond to the non-illuminated areas of the original light image. A reverse visible powder image is a developed image wherein the developed areas correspond to the lighted areas of the original light image. By adjustment of the biasing voltage, any desired contrast characteristic over a wide range may be obtained for either the direct or the reverse image. Thus, one may simply and quickly adjust an electrostatic printing apparatus to produce line prints of high contrast value, continuous tone prints of intermediate contrast value and, in each case, the print may be direct or reverse.

Any photoconducting layer usable in electrophotography may be used in the invention. Some of the useful photoconducting layers are described by C. J. Young and H. G. Greig in "Electrofax-Direct Electrophotography Printing on Paper," RCA Review, December 1954, volume 15, No. 4, pages 469 to 484; by E. Wainer, "Phosphor Type Photoconducting Coatings for Continuous Tone Electrostatic Electrophotography," Photographic Engineering, volume 3, No. 1, 1952, pages 12 to 22; and by A. Middleton in U.S. Patent No. 2,663,636, issued December 23, 1953.

Some suitable photoconducting coatings are photoconducting zinc oxide (AZO 33 marketed by the New Jersey Zinc Co., Palmerton, Pa.) dispersed in a silicone resin, photoconducting zinc selenide (Mallinkrodt No. 8856 marketed by the Mallinkrodt Chemical Works, New York, N.Y.) dispersed in a silicone resin, photoconducting zinc sulfide (Cryptone ZS 800 marketed by the New Jersey Zinc Co., Palmerton, Pa.), and panchromatically-sensitive zinc oxide prepared according to either U.S. Patent No. 2,727,807 or 2,727,808 to S. M. Thomsen dispersed in a silicone resin. In place of a silicone resin one may substitute a polystyrene resin, a polyvinyl acetate resin, a polyvinyl-chloride acetate resin, carnauba wax or other electrically-insulating, film-forming vehicle.

A preferred composition may be prepared by intimately mixing 100 grams of a photoconducting zinc oxide, such as Florence Green Seal No. 8 marketed by the New Jersey Zinc Company, Palmerton, Pa. with 65 grams of a 60% solution of a silicone resin in xylene (such as GE SR-82 marketed by the General Electric Co., Silicone Products Division, Waterford, N.Y.), and 85 grams of toluene.

After ball-milling to obtain a smooth, uniform consistency, the mixture is coated on the surface of a paper web and dried. Any standard coating technique may be used such as flowing, spraying dipping, spin-coating, or brushing on.

In addition to the vehicle-bound type coatings described, one may use coatings having no vehicle such as sulfur, anthracene or selenium. Where selenium is used, the magnetically responsive carrier particles should be non-conducting such as a ferrosin powder or a resin-coated iron powder.

An essential part of the developing procedure is that it must be carried out during the decay of conductivity of the photoconducting layer. Referring to Figure 3, there is shown a plot of conductivity in an incremental area of the photoconducting layer 23 of Figures 1 and 2 with respect to time. The photo-conducting layer is stored in darkness for the period 0-1 and reaches a steady state of minimum conductivity as shown by A-B. Light is turned on during the period 1-2, which is the period of exposure to the light image, during which the conductivity rises to a maximum value as shown by B-C. After the light is turned off at 2, the conductivity begins to fall to a minimum value during the period 2-3 as shown by C-D. It is during the interval 2-3, 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. The photoconducting coating of the example has a very long period of decay and development may take place during a period of at least 16 hours after exposure to the light image. However, development preferably takes place within a period of 30 minutes after exposure to the light image.

The developer powder particles of the developer mix may be chosen from a large class of materials, for example; zinc, copper, carbon, sulphur, gum copal, gum sandarac, nylon, polystyrene, sealing wax and other natural or synthetic resins of mixtures thereof. The developer powder particles may be coated with a thin layer of a material for the purpose of modifying the physical or electrical properties of the developer powder. It is preferred, however, to use a pigmented thermoplastic synthetic resin.

A preferred developer powder of the example 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 Company, Clairton, Pa., and 12 grams of Carbon Black G marketed by the Eimer and Amend Co., New York, N.Y., are thoroughly mixed in a stainless steel beaker at about 200° C. The mixing and heating should

5

be done in as short a time as possible. The melt is poured upon 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 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 iron powder. It therefore will develop the more insulating areas of a latent conductivity pattern with a positive biasing voltage applied to the magnetic brush.

The magnetic carrier particles of the developer mix may be chosen from a large class of powdered magnetically-attractable materials such as iron, steel, alloys of aluminum, nickel and cobalt and other magnetic materials.

A preferred carrier material for the developer mix of the example consists of "alcoholized iron," that is, iron particles free from grease and other impurities soluble in alcohol. These iron particles are preferably relatively small in size, being in their largest dimension about 0.002 to 0.008 inch. Satisfactory results are also obtained using a carrier consisting of iron particles of a somewhat wider range of sizes up to about 0.001 to 0.020 inch. It is preferred to utilize a permanent bar magnet for providing the magnetic field for maintaining the developer mix in a loose mass. However, other structures may be used, such as electromagnets or other magnetic field producing means. Similarly, the biasing voltage may be applied to the mass of developer mix of the brush as shown in Figure 2 or may be applied to the backing plate 44a with the developer mix connected to ground, as subsequently described in Figure 4.

A positive or a negative voltage may be used to bias the magnetic brush so long as there is no electrical breakdown in the brush or in the photoconducting layer 23 upon which the latent conductivity pattern resides. It is preferred, however, to use a voltage between -1500 to -500 and +500 to +1500 volts D.C. The optimum range of voltages depends upon the thickness and the electrical properties of the photoconducting layer 23.

Development occurs instantaneously with ± 1500 volts between the brush 29 and the backing 21. In order to remove spurious deposits of developer powder in the background areas, the voltage may be reduced to about 500 volts in the same polarity after the initial deposit of developer powder. Various rates of lowering the voltage may be used so long as the higher voltage preceded the lower voltage.

Referring to Figures 4 and 5, the improved methods and means of the invention may be embodied in an improved continuous electrostatic printing process and apparatus. A continuous web comprising a paper backing 51 having on one surface thereof a photoconducting insulating coating 53 comprising a powdered photoconductor, such as zinc oxide, dispersed in an electrically-insulating, film-forming vehicle is unwound from a roll 55.

The continuous web next passes to a station where a light image is produced upon the surface of the photoconducting coating 53, for example, by projection from a photographic transparency image by means of a projector 57. The photoconducting insulating layer 53 now has therein a latent conductivity pattern substantially corresponding to the light image which was projected thereon.

The continuous web next advances to a station where the latent conductivity pattern is developed by the method of the invention by contact with a first magnetic brush. A grounded rotary pole piece 63a of a magnetic structure is provided with spaced parallel inclined elliptical discs 61a facing the photoconducting coating 53. A magnetic field is maintained between a fixed magnetic pole piece 45a spaced from the elliptical discs 61a and on the opposite side of the web through magnetic pieces 47a and 49a and through the gap therebetween. A reser-

6

voir 65a holds a quantity of developer mix in contact with the discs 63a. A shield 44a located between the fixed pole piece 45a and the web is maintained in contact with or closely spaced behind the paper backing 51 and is connected to a voltage source 31a through a double-pole, double-throw reversing switch 33a and a potentiometer 35a. The switch 33a and the potentiometer 35a are adjusted to provide the desired biasing voltage upon the shield 44 for example, a voltage of +1500 volts.

As the rotary pole piece 63a rotates in a clockwise direction as viewed in Figure 4, developer mix forms on the periphery of the discs 61a in brush-like filaments 69a and is carried upwardly and swept across the surface of the photoconducting insulating coating 53 passing the station. Developer powder particles 73 deposit upon areas previously unilluminated producing a reverse visible powder image on the photoconducting coating 53 in substantial configuration with the latent conductivity pattern. According to the invention, direct or reverse visible powder images may be produced and the background color value and the contrast value of the visible image may be varied by adjusting the biasing voltage to the shield 44 as previously described in Figure 2.

The continuous web now passes to a station where the photoconducting coating 53 is contacted with a second magnetic brush. The second magnetic brush has the same structure and operates in the same manner as the first magnetic brush except that the biasing voltage on the shield 44b is maintained at about +500 volts. The function of the second magnetic brush is to clear away any spurious deposit of developer powder without disturbing the powder image 67.

The continuous web bearing the visible powder image 73 thereon now passes to a station where the visible image is fixed to the photoconductive coating 53. For this purpose a radiant heater comprising a resistance wire 79 connected to a voltage source 75 through a potentiometer 77. The resistance wire 79 is maintained in closely spaced relationship with the visible powder image. Heat radiated from the wire 79 softens the thermoplastic resin of the developer powder causing it to adhere to the photoconducting coating 53. The visible powder image may be fixed to the photoconducting layer 53 by other means for example, by spraying with an adhesive or by coating with a softener for either the photoconductor 53 or the developer powder particles. The visible powder image may also be transferred to another surface and fixed thereon by any convenient means. The continuous web bearing the fixed visible image is now wound upon the roll 56. The continuous web of course, may be cut into convenient lengths and stacked in piles or utilized directly.

There have been described improved methods and means of photoconductive photography including improved methods and means for developing latent conductivity patterns. There have also been described methods and means for producing direct or reverse visible images and for controlling the contrast value of the visible powder image developed according to an improved photoconductive photography process.

What is claimed is:

1. An electrostatic printing process comprising the steps of producing a conductivity pattern in a photoconducting insulating layer consisting of a finely-divided photoconductor dispersed in an electrically-insulating vehicle by exposing said layer to a light image before any electrical field is established through said layer, then magnetically transporting across said conductivity pattern a dry physical mixture of loose, movable particles of electrostatically-attractable powder and separate electrically conductive magnetically-attractable carrier particles by subjecting said magnetically attractable particles to a magnetic field brought across said conductivity pattern, said carrier particles and powder particles having a triboelectric relationship of opposite polarity, the powder particles thereby being electrostatically-charged through tri-

boelectric action by contact with the carrier particles to adhere electrostatically to the surface of the carrier particles, and during said transporting step applying a biasing voltage to said electrically conducting particles with respect to the opposite surface of said layer to establish through said layer a unidirectional electric field and to cause powder particles to become attracted to said insulating layer and to adhere thereon in substantial configuration with said conductivity pattern.

2. An electrostatic printing process comprising the steps of producing a conductivity pattern in a photoconducting insulating layer consisting of a finely-divided photoconductor dispersed in an electrically-insulating vehicle by exposing said layer to a light image before any electrical field is established through said layer then magnetically transporting across said conductivity pattern a dry mixture of loose, movable particles of electrostatically-attractable powder and separate electrically conductive magnetically-attractable carrier particles by subjecting said magnetically-attractable particles to a magnetic field brought across said conductivity pattern, said carrier particles and powder particles having a triboelectric relationship of opposite polarity, the powder particles thereby being electrostatically-charged through triboelectric action by contact with the carrier particles to adhere electrostatically to the surface of the carrier particles, spacing an electrode from said mixture and on the side of said insulating layer opposite to said mixture, and applying a biasing voltage between said electrode and said magnetically attractable particles during said transporting step to establish a unidirectional electric field through said insulating layer and to cause powder particles to become attracted to said insulating surface and to adhere thereon in substantial configuration with said conductivity pattern.

3. An electrostatic printing process comprising the steps of producing a conductivity pattern in a photoconducting insulating layer consisting of a finely-divided photoconductor dispersed in an electrically-insulating vehicle by exposing said layer to a light image before any electrical field is established through said layer, then magnetically transporting across said conductivity pattern a dry mixture of loose, movable particles of electrostatically-attract-

able powder and separate electrically-conductive magnetically-attractable carrier particles by subjecting said magnetically-attractable particles to a magnetic field brought across said conductivity pattern, said carrier particles and powder particles having a triboelectric relationship of opposite polarity, the powder particles thereby being electrostatically-charged through triboelectric action by contact with the carrier particles to adhere electrostatically to the surface of the carrier particles, spacing an electrode from said mixture and on the side of said insulating layer opposite to said mixture, applying a biasing voltage between said electrode and said magnetically-attractable particles during said transporting step to establish a unidirectional electric field through said insulating layer and to cause powder particles to become attracted to said insulating surface and to adhere thereon in substantial configuration with said conductivity pattern, and then repeating said contacting step with a lower biasing voltage applied.

4. The process of claim 2 wherein said insulating layer comprises photoconducting zinc oxide dispersed in a silicone resin.

5. The process of claim 3 wherein said insulating layer comprises photoconducting zinc oxide dispersed in a silicone resin.

6. A method according to claim 2 wherein said biasing voltage is between 500 and 1500 volts.

7. A method according to claim 3 wherein said biasing voltage is about 1500 volts and said lower biasing voltage is about 500 volts.

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2,408,143	Huebner	Sept. 24, 1946
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2,803,177	Lowrie	Aug. 20, 1957

OTHER REFERENCES

RCA Review, December 1954, pp. 469 to 484.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,956,874

October 18, 1960

Edward Charles Giaimo, Jr.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, list of references cited, under the heading "UNITED STATES PATENTS", add the following:

2,786,439	Young-----	Mar. 26, 1957
2,786,440	Giaimo-----	Mar. 26, 1957
2,808,328	Jacob-----	Oct. 1, 1957
2,845,348	Kallman-----	July 29, 1958

same column 8, under the heading "OTHER REFERENCES", add the following:

Wainer, Photographic Engineering, Vol. 3,
No. 1, pp. 12-22 (1952).

Signed and sealed this 18th day of April 1961.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents