

Oct. 9, 1973

B. L. SHELBY

3,764,313

ELECTROGRAPHIC FIELD ELECTRODE

Filed April 29, 1969

2 Sheets-Sheet 1

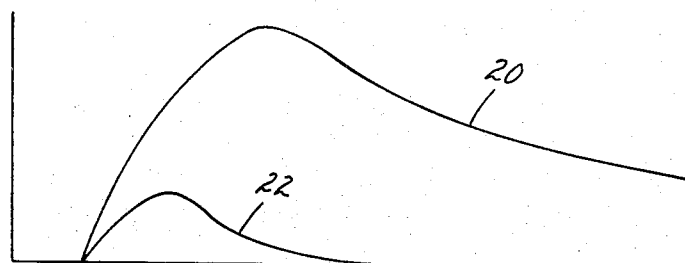
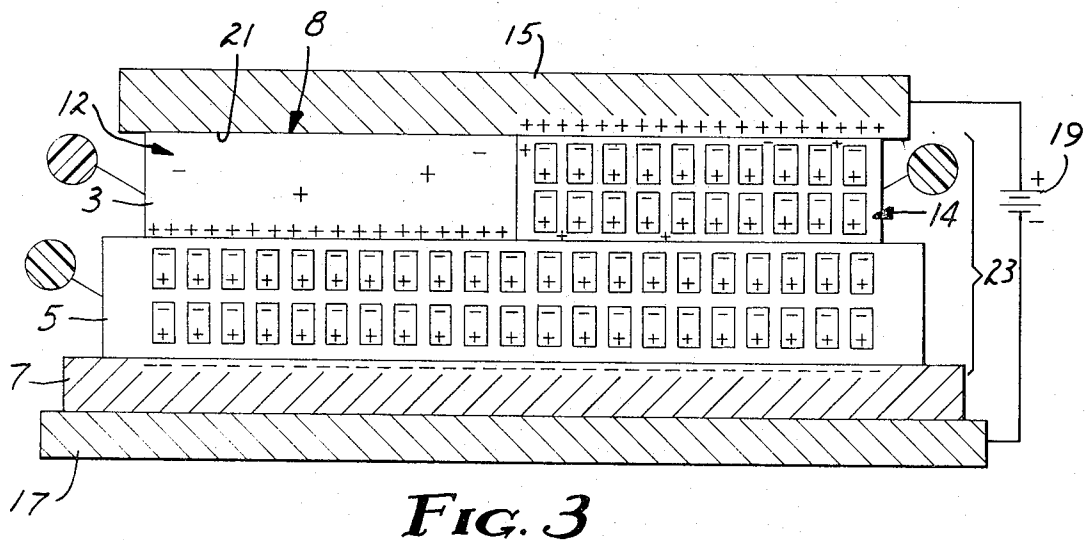
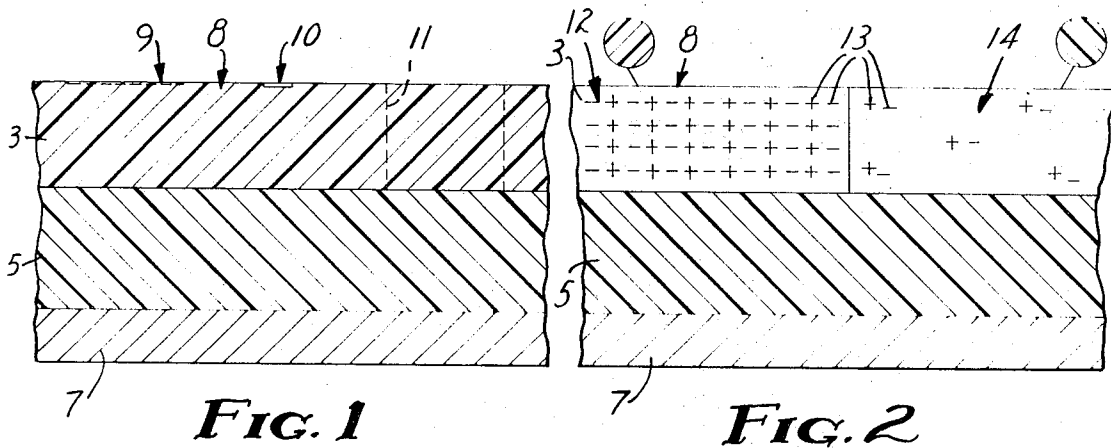


FIG. 4

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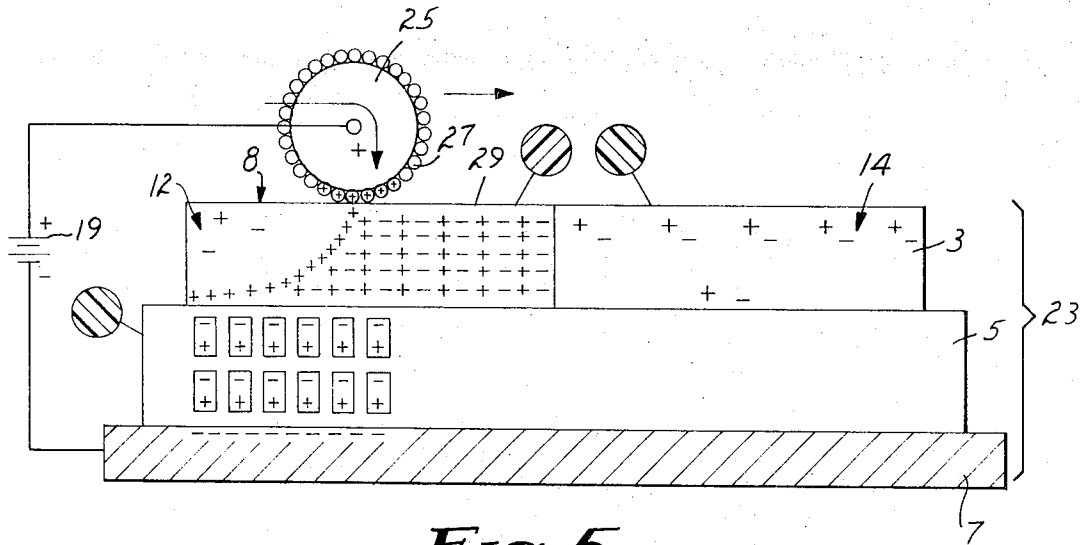


FIG. 5

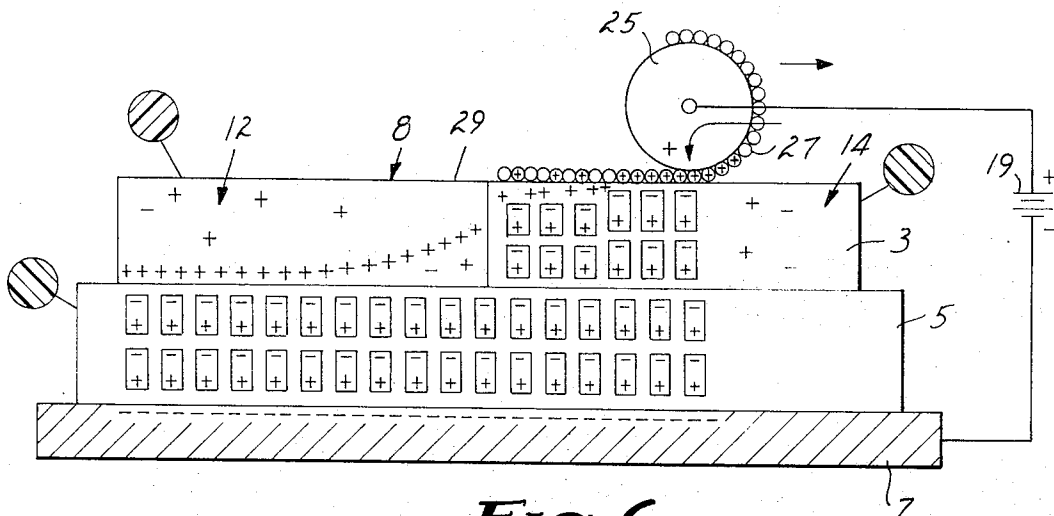


FIG. 6

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3,764,313

ELECTROGRAPHIC FIELD ELECTRODE

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Continuation-in-part of application Ser. No. 663,818, Aug. 28, 1967, now Patent No. 3,563,134, which is a continuation-in-part of abandoned applications Ser. No. 403,737, Oct. 14, 1964, and Ser. No. 567,170, July 22, 1966. This application Apr. 29, 1969, Ser. No. 820,062

Int. Cl. G03g 5/02, 5/06, 5/08

U.S. Cl. 96—1.5

16 Claims

ABSTRACT OF THE DISCLOSURE

A multilayered sheet construction for use in a dynamic electrographic process as the ultimate copy or as an intermediate for preparing copies, such sheet having an image layer capable of providing a differentially conductive image pattern which is developable by conductive particulate under a development voltage, a dielectric layer bonded to the image layer which is of a thickness and conductivity whereby charge flow through the conductive regions of image layer is controlled to reduce powder deposition in background areas, and a conductive layer bonded to the dielectric layer.

This application is a continuation-in-part of my copending application Ser. No. 663,818, filed Aug. 28, 1967, now U.S. Pat. No. 3,563,134, which in turn is a continuation-in-part of my copending application Ser. No. 403,737, filed Oct. 14, 1964, now abandoned, and my application Ser. No. 567,170, filed July 22, 1966, now abandoned.

This invention relates to the field of reproduction more particularly, it relates to a multilayered sheet construction more descriptively denominated a field electrode which can be imaged to provide a differentially conductive pattern for use in reproduction procedures such as the electrographic techniques described in the above mentioned application Ser. No. 663,818.

The electrographic process for which the sheet construction of this invention is especially adapted involves providing the sheet (field electrode) with a latent image in the form of a differentially electronically conductive pattern such as by exposure of the sheet bearing a dark adapted photoconductive surface coating to a light image or light pattern, and then developing the latent image to provide either a positive or negative copy of the pattern. Development is accomplished by contacting the patterned sheet with conductive developer material applied from a conductive applicator surface to which it is adhered, such contact being undertaken with simultaneous imposition of a uniform direct current electrical potential between the patterned photoconductive sheet and the conductive surface bearing the developer whereby the developer powder is transferred to the sheet either in the conductive or non-conductive areas as determined by the method of development.

The influence of the electrical potential is maintained during separation of the sheet from the source of supply of the developer, and following such separation, the developer can either be fixed on the sheet surface to provide a direct copy, or the developer can be transferred from the sheet to another substrate. Thus in the outlined reproduction process, the sheet can be the ultimate copy or an intermediate for use in providing further copies.

Deposition of conductive developer powder on the field electrode primarily occurs as a result of the establishment of an electrical potential difference which in all practical situations is a transient potential difference across the

2

field electrode-conductive powder interface. By "transient" is meant the fact that the potential difference exhibits a surging effect which rises and drops off while a given unit area of the field electrode is in electrical contact with the applicator bearing development powder during development. This transient potential difference is largest in regions of relative non-conductivity of the field electrode where the charge flow resulting from the applied potential cannot flow freely across the interface between the conductive powder and field electrode. Unless otherwise stated, the term "charge" as used herein means charge induced in relatively conductive elements as a result of an electric current of charge carriers moving under the influence of an applied potential impressed upon the circuit elements as opposed to electrostatic charges such as result from triboelectric or corona or other electrostatic charging techniques. In relatively conductive regions, on the other hand, relatively free current flow occurs across the interface and the requisite potential difference establishing a force sufficient to overcome the force holding the powder to the applicator is not generated. The rate of powder deposition (the amount of powder deposited per coulomb of charge flow) for a given development time is inversely proportional to the conductivity at the surface of the image layer.

However, a countervailing factor to non-deposition of developer powder in the conductive regions of the image layer is the direct dependence between deposition and the amount of charge flow in a given unit area for a given development time. Thus, deposition in the conductive regions is favored because the charge flow is far greater in the conductive regions. The result may be a small yet deleterious amount of powder being unavoidably transferred to the conductive, background regions absent some means of controlling or regulating the total charge flow. This is the case with field electrodes consisting of a photoconductive layer bonded directly to a conductive layer (e.g., zinc oxide in an insulating binder bonded to aluminum foil) wherein needlessly high developer deposition occurs in the conductive areas due to this dependency on total charge flow, resulting in high background and low contrast of the copy.

Moreover, the time in which the developer material is in contact with such non-regulated field electrodes, as when a roller bearing developer material on its outer surface is passed over the field electrode surface, will be critical as will be the development voltage, since both directly affect the total charge passed. Furthermore, if electrical breakdown occurs in conductive regions of the photoconductive layer, a large current will flow leaving spots of developer or marking material deposited in areas which should remain white.

Thus, a non-regulated field electrode lacks sensitometric qualities essential to high quality duplication and imposes rather stringent requirements upon the processing conditions which can be employed. Given the highly competitive nature of duplicating techniques, these drawbacks can prove fatal to even a modicum of commercial acceptance, particularly in the area of office duplication where processing is not subject to stringent care and control.

It is the primary object of this invention to provide a field electrode for use in an electrographic process which will exhibit excellent sensitometric qualities, i.e., high resolution, clean background, high image density, and contrast control. Another object is the provision of a receptor which will not be subject to electrical breakdown under the necessary processing conditions thereby affording uniform development with no visible breakdown spots thus affording the option to re-use the field electrode. Another object is the provision of a field electrode which

will provide acceptable reproduction over a wide range of input image densities and processing conditions resulting in low background and sufficient resolution.

These and other objects which will be more apparent hereinafter are provided by the present invention which is a sheet construction comprising an image layer capable of providing a differentially conductive image pattern, a dielectric layer bonded to said image layer, said dielectric layer being of a thickness and resistivity capable of allowing only a predetermined amount of electrical charge to pass in each unit area of said image layer under said development voltage, and a conductive layer bonded to said dielectric layer, said conductive layer having a conductivity such that substantially no voltage drop occurs across the conductive layer under said development voltage. It is the dielectric layer as described herein which, in cooperation with the image layer and conductive layer, provides the control over charge flow in the conductive regions of the field electrode to prevent the developer powder deposition in unwanted, background areas.

In another embodiment of this invention, an electrographic process is provided which comprises (1) providing an image pattern defined by relatively conductive and non-conductive regions on at least the surface of the image layer of the field electrode as defined above, (2) contacting a unit area of said image pattern with an electrically conductive applicator surface bearing electrically conductive developer material, (3) concurrently with said contact imposing a direct current electrical potential between said conductive layer and said electrically conductive applicator surface in said unit area to create a transient potential difference in said unit area between said developer material and said relatively non-conductive regions, (4) maintaining said contact for a period sufficient to permit said transient potential difference to assume a level where it exerts a transfer force greater than the applicator force holding said developer material on said electrically conductive applicator surface, and (5) breaking the contact between said applicator surface and said image layer in said unit area while said transfer force exerted by said transient potential difference in said relatively non-conductive regions is greater than said applicator force, whereby said developer material transfers to the surface of said image layers in said relatively non-conductive regions within said unit area, and repeating steps (2)-(5) until the aggregate of unit areas includes all of said image layer desired to be developed.

While the field electrode is preferably in the form of a flexible sheet, it is to be understood that any construction embodying the combination of layers defined herein is suitable and contemplated within the practice of this invention. Thus, the field electrode may be a rigid structure such as is obtained from a metal plate conductive layer on one major surface of which is located the dielectric layer, and over which is located the image layer.

In order to better understand the invention, reference is made to the accompanying drawings wherein:

FIG. 1 is an elevational cross section of a field electrode of this invention;

FIG. 2 is an elevational cross section of an embodiment of the field electrode of this invention showing the differentially conductive pattern prior to development;

FIG. 3 is a diagrammatic view in cross section showing the field of electrode of FIG. 2 under a development voltage between conductive plates;

FIG. 4 is a graphic representation of two curves representing the transient potential across the conductive developer powder-field electrode surface interface with time under a development voltage in the practical case of other than perfect conductive and non-conductive or insulating regions of the field electrode surface; and

FIGS. 5 and 6 are diagrammatic views in cross section illustrating the development of a differentially conductive pattern created with a field electrode of this invention.

Referring to FIG. 1, the field electrode 1 has an image

layer 3 bonded to a dielectric layer 5 which in turn is bonded to a conductive layer 7. The basic requirement of image layer 3 is that at least the free surface thereof be capable of providing a differentially electronically conductive pattern upon imaging. The term "differentially electronically conductive pattern" is used in the sense that imaging of image layer 3 results in a pattern defined by regions of relative conductivity and regions of relative non-conductivity under the process conditions employed, which regions together correspond to the record to be reproduced. To be considered a region of relative conductivity, such region should be capable of accepting electrical charge within the duration of the development time from a conductor brought into contact with it under the influence of a suitable impressed electrical field. That is to say, it should be capable of allowing a real electrical current of charge carriers to flow across the interface between the conductor or conductive powder and the field electrode under the influence of an electrical potential impressed across the circuit elements. In image layer 3, three such regions are depicted: region 9 wherein the relative conductivity is at the free surface 8 of image layer 3 (e.g., a surface state); region 10 wherein the relative conductivity extends transversely from free surface 8 only an infinitesimal distance; and region 11 wherein the relative conductivity extends transversely from free surface 8 completely through layer 3. The dielectric layer 5 makes intimate surface contact with the underside of image layer 3 and the conductive layer 7 in turn makes intimate surface contact with the other surface of dielectric layer 5.

To be considered a suitably conductive region for the purposes of this invention, the conductivity need only be exhibited at the electric fields impressed across the interface during development of the field electrode. For example, regions 9-11 may have a strongly field dependent conductivity, being insulating at low electric fields, but being conductive at the electric fields impressed upon them during development. Thus, regions 9-11 could have a barrier to charge flow at the interface at low electric fields, but this barrier could be overcome by the impressed electric fields at the interface during development, allowing charge interchange across the interface under these field conditions.

In the same manner, the relative non-conductivity of image layer 3 refers at least to the conditions at the surface under the impressed electric fields during development.

FIG. 2 illustrates a field electrode construction which has been imaged to provide a region 12 of relative conductivity extending through image layer 3 and a region 14 of relative non-conductivity also extending through image layer 3; regions 12 and 14 together providing a differentially electronically conductive pattern illustrated by the greater number of charge carriers 13 in region 12 versus region 14.

In order to illustrate the interchange of charge across the interface of the field electrode under an impressed electric field, FIG. 3 diagrammatically shows the field electrode of FIG. 2 sandwiched between two conductive plates 15 and 17. A unidirectional electrical potential from a conventional source 19 is applied to impress an electrical field across the field electrode. A current will flow in the series electrical circuit which is referred to as a real current in conductive parts of the circuit (source 19, conductive plates 15 and 17, conductive layer 7, and conductive region 12) and as a displacement current in the dielectric or insulating parts of the circuit (dielectric layer 5 and nonconductive region 14). Charge will flow freely across the interface 21 of the conductive region 12 and conductive plate 15 and will continue to travel through the conductive region 12, coming to rest at the dielectric layer 5. Charges of the opposite sign come to rest in layer 7 on the opposite side of the dielectric layer 5, and a polarization is induced in the dielectric layer. Charge will not flow across the interface 21 in the non-

5

conductive region 14, but will stop on the surface of the conductive plate 15. Again, charges of opposite sign are induced in conductive layer 7 at its interface with the dielectric layer beneath this region. Polarization is also induced in both the dielectric layer 5 and the nonconductive region 14 of image layer 3.

In the case where region 14 is not perfectly nonconducting but only less conducting than region 12, which is true for all practical cases, a transient potential exists across the interface 21 in region 14 since the charge is impeded from flowing freely across the interface, but will ultimately cross the interface and drift to the surface of layer 5 (more slowly than in region 12). Here, the relative time dependence of the potential across the interface 21 is shown graphically in FIG. 4 as curve 20.

Likewise, when region 12 is not perfectly conducting but only more conducting than region 14, as in all practical cases, a transient potential will appear across the interface 21 in region 12 also, but will be smaller and of shorter duration than for region 14 as shown graphically in curve 22 (for region 12) and curve 20 (for region 14) of FIG. 4. By the expedient of holding the developer powder on the applicator with a force greater than the force asserted by the potential difference at the interface of the field electrode in conductive regions at the time of separation of the field electrode from the powder, but less than the force asserted by the potential difference in nonconductive regions, selective deposition can be effected. Preferably, the holding force of powder to applicator is magnetic in nature. Since only transient potential differences are involved, differential development takes place during the presence of this transient potential difference, and thus development time is very important.

To illustrate the differential development of the differential conductivity pattern, FIGS. 5 and 6 diagrammatically show a field electrode 23 being progressively developed by passing a roller 25 bearing an electrically conductive powder 27 over the field electrode 23. During such development, potential source 19, connected to the conductive layer 7 and the conductive powder bearing roller 25, impresses a field across the field electrode 23 and the powder 27 between the roller 25 and the field electrode 23. The powder 27 is electrically conductive itself, or at least semi-conductive, at the electric fields impressed. In most cases, the powder 27 has a strongly field-dependent conductivity and is more conductive than either the conductive or nonconductive regions of image layer 3, under the fields impressed during the early part of the development transient. At low electric fields, the powder is much less conductive than it is at high electric fields.

In FIG. 5, as the roller 25 passes across the conductive part 12 of the field electrode 23, current flows as described in conjunction with FIG. 3, and charge interchange takes place more or less freely across the interface 29, resulting in a very small transient potential difference of very short duration across this interface 29 and thus little or no force exists between the particles of conductive powder 27 and the field electrode 23 in this region. The charge continues to flow through the image layer 3 as before coming to rest on the interface between the layers 5 and 3. Dielectric layer 5 appears as a charged capacitor in regions where the roller has passed over. It is to be understood that charges of a given sign moving in a given direction are to be taken as equivalent to charges of the opposite sign moving in the opposite direction. Thus, if the conductive region shown were either an n-type conductor or semiconductor or a p-type conductor or semiconductor, or both, the same illustration would suffice.

Referring to FIG. 6, as the roller 25 passes over the relatively nonconductive region 14, which in all practical cases is not perfectly nonconductive but merely semi-conductive (in any case less conductive than region 12), a transient potential difference will appear across the powder-field electrode interface 29 as discussed earlier and

6

graphically shown by curve 20 in FIG. 4. This results in a transient force exerted on the powder toward the field electrode proportional to the potential difference. If powder is to be deposited in this case, the roller must move at the proper speed such that the potential difference across the interface is still large enough at the instant the powder must separate from either the roller or the field electrode (i.e., at the trailing edge of the development nip) so that the powder adheres to the field electrode rather than to the roller. As is illustrated, the development voltage is applied continuously and is present at the time of separation. Since both the roller and the powder are conductive at the development fields used in the process, there is free interchange of charge between them, and hence little attraction between them, at least it is weaker than the attraction between the powder and the less conductive areas 14 of the field electrode at the time of separation of the powder from the roller.

While the foregoing discussion primarily relates to a field electrode wherein the conductive regions 12 extend entirely through the exposed, differently conductive image layer 3, it is to be understood that the principles are generally applicable to embodiments wherein the conductive regions do not extend through the image layer 3, such as regions 9 and 10 of FIG. 1. Thus, the determinative factor in gaining selective deposition of powder lies in the degree of freedom of charge interchange across the interface between the conductive powder and the surface of image layer 3, as current flows in the development circuit. If charge can flow freely across the interface, even if it is only from the powder to the surface of the image layer, there will be substantially no powder deposition in these areas since a sufficient potential difference cannot be built up across the interface and therefore there will be an insufficient force on the powder drawing it away from the applicator and toward the surface of the field electrode.

However, as noted above, for a given development time powder deposition is also directly proportional to the charge flow in the circuit per unit area, resulting, in the absence of control, in a small yet deleterious amount of powder being deposited in the conductive areas. It is the dielectric layer, in combination with the image and conductive layers, which provides a means for controlling the total charge flow and alleviation of the attendant problems.

The dielectric layer can be thought of as a longitudinally extending distributed capacity in series between the image layer and the conductive layer. It will thus serve as a charge shut-off valve allowing only a predetermined amount of charge to pass in each unit area of the image layer under the given development voltage. Since the lateral conductivity (parallel to the surface) of both the dielectric layer and the nonconductive region of the image layer is very low, adjacent unit regions of the dielectric layer will act independently of each other; i.e., regions of the dielectric layer beneath conductive regions will charge rather quickly, shutting off the current flow in these regions, while regions of the dielectric layer beneath nonconductive regions will charge more slowly. Both regions thus receive roughly the same charge during the total development time, which is sufficiently long for both regions to charge almost to the development voltage.

Eliminating the disparity in charge flow per unit area between the conductive and nonconductive regions will reduce the background and consequently enhance the contrast, as explained above. Furthermore, the time spent in the nip and the exposure time are far less critical than when no dielectric layer is present since the total charge flow is now regulated more or less independently of the above variables. The time in the nip and the exposure are still important, but far less critical. This results in greatly increased processing latitude, i.e., the process can be conducted free from narrow limits.

The dielectric strength and the ability of the dielectric layer to serve as a current shut-off valve are related to the thickness of the dielectric layer. Taking the dielectric

strength of good dielectric or insulating materials to be about 3×10^6 volts per centimeter, and an average development voltage of about 600 volts and above, dielectric layers of at least 2 microns are desired with a range of from 2 to about 125 microns being preferred. Preferably, the dielectric layer is substantially uniform in thickness. The thicker dielectric layers are necessary for the development voltages at the upper end of the range of useful development voltages and also for dielectric materials which have lower dielectric strength than that quoted above. For example, a 2 micron polyester layer with a dielectric strength of about 3×10^6 volts per centimeter would be useful for development voltages up to 600 volts while a 4000 volt development voltage would require a polyester layer of at least about 13 microns to prevent electrical breakdown. If the dielectric strength of the layer were only one-fifth that given in the example, the thickness of the dielectric layer would have to be increased to 10 microns for development voltages of about 600 volts, and to about 65 microns for development voltages around 4000 volts. Considering the charge limiting characteristics of the dielectric layer, the smaller the capacity per unit region (thicker dielectric layers), the more equal will be the total charge flow in both the conductive and nonconductive regions of the image layer for a given development time.

Experience has shown that 25 micron dielectric layers are superior to 13 micron and 6 micron layers in this respect (less background, higher contrast, wider processing latitude), but increasing the thickness beyond 25 microns has not given the degree of improvement found in advancing from 2 to 25 microns, probably because the total charge flow in conductive and nonconductive regions is almost equal at 25 microns thickness for the normal development times of from about 10 to 50 milliseconds. Development time is the time each unit area of the field electrode spends in the development nip, i.e., the time each unit area spends in contact with the powder which fills the gap between the field electrode and the development roller and is still in electrical contact with the development roller. If considerably shorter development times are involved, such as from about 0.5 to 10 milliseconds (due to faster processing speeds), then one would also see a larger difference between the thicker dielectric layers, e.g., between 25 microns and 50 microns. Thus, whereas a dielectric layer of at least 2 microns is suitable, and a range of from 2 to about 125 microns is preferred, within the latter range resides the most preferred range of from about 20 to about 50 microns wherein the widest processing latitude and lowest reasonable development voltages can be gained for typical processing conditions.

In addition, to achieve the desired shut-off action, the direct current conductivity of the dielectric layer should be low enough to insure negligible charge leakage through the dielectric layer during the time spent in the development nip. This condition is satisfied where: $(8.85 \times 10^{-14}) \rho \epsilon \geq 10 \text{ times } t_{\text{nip}}$ where ρ is the resistivity in ohm-cm., ϵ is the dielectric constant of the dielectric layer, and t is the time spent in the development nip in seconds. Considering practical minimum nip times, it is calculated that the conductivity of the dielectric layer should be about 10^{-11} (ohm-cm.)⁻¹ or lower, and preferably 10^{-12} or lower, a conductivity fulfilled by most good dielectric or insulating materials. It is preferred that the dielectric layer exhibit such conductivity independent of the ambient conditions, i.e., temperature and relative humidity. In any case the conductivity of the dielectric layer should be at most about .1 of the conductivity of the conductive layer.

A variety of materials satisfy the requirements for the dielectric layer of this invention including polyesters such as that available commercially under the trade name Mylar, polypropylene, polycarbonate, cellulose acetate, and polystyrene.

The image layer of the field electrode of this invention should provide a differentially conductive pattern wherein the conductive regions are at least twice as conductive

as the nonconductive regions, preferably at least 10 times as conductive. The relatively conductive regions of the image layer (containing the conductive pattern) should be as conductive as possible and at least have a maximum resistivity at the surface (transverse resistivity at the surface, which applies to all three types of conductive regions shown in FIG. 1) of 10^{15} ohm-cm., preferably 10^{14} ohm-cm. The relatively nonconductive regions should generally have a minimum resistivity at the surface of 10^7 ohm-cm., although for special conditions, a resistivity of 10^4 or 10^5 ohm-cm. would be suitable. These resistivity values are measured under an electric field and for an applied time corresponding to that to be used in the process, and it is to be remembered that the conductive regions are at least twice as conductive as the nonconductive regions within the above over-all ranges, and the conductive regions are at least about 10 times as conductive as the dielectric layer.

For best results, the limits of transverse resistivity at the surface of both the nonconductive regions and the conductive regions of the electrode are between about 10^7 and 10^{14} ohm-cm.

The differentially electronically conductive pattern may be obtained by various methods such as by the use of a semi-conductive layer, a photoconductive insulating layer, or a conductive photosensitive layer which becomes more insulating upon illumination. In the use of a photoconductive layer on an insulating sheet to create the differentially conductive pattern, the resistivity will depend upon several factors such as the resistivity characteristics of the photoconductor and binder, the applied electrical potential, and the intensity and type of radiation used during the exposure step of the process.

It has been found that a number of materials will be suitable as an image layer even though they do not show good bulk photoconducting properties. Titanium dioxide is an example. With such photosensitive materials, illumination probably causes photodesorption of oxygen from the photosensitive particle with a resultant change in conductivity at the surface. Exemplary of an image layer capable of providing a differential conductivity pattern transversely through such layer is a photosensitive layer comprising a zinc oxide photoconductor embedded in suitable resin binder such as a styrene-butadiene copolymer. Another example is a pattern, corresponding to the record to be reproduced, of conductive graphite in a water dispersion, or conductive silver paint applied to a dielectric layer backed by a suitable conductive layer. In embodiments such as these, the image layer is not continuous as in the preferred case of a photoconductor embedded in a resin to provide a coating over the dielectric layer. The pattern may be applied by a number of conventional techniques including painting or printing. A suitable aqueous graphite dispersion is available commercially under the trade name Aquadag. A suitable silver paint is available commercially under the trade name Silver Print No. 21-2. In these latter embodiments, the powder is deposited everywhere on the insulating surface except where the conductive material is present.

Other suitable photoconductive materials include CdS; organic photoconductive materials such as oxadiazoles and amidoanthraquinones; or halogenated hydrocarbons such as hexabromoethane or iodoform which produce free radicals upon exposure to actinic light.

Heat sensitive image layers may also be employed including hydrated inorganic compounds such as aluminum or silica in a polymeric binder, the compounds increasing their resistivity when heated. The heat source can be a hot stylus or infrared radiation such as is provided in commercial thermographic copying machines.

The conductive layer of the field electrode of this invention may be supporting or non-supporting, for example, a thin vapor coated metal layer or a thicker conductive paper support. The conductivity of this layer must be such that no more than a small voltage drop occurs

across it when the developing current passes through it. Small in this sense is relative to the voltage drop in other parts of the circuit through which current passes. Preferably, the voltage drop across the conductive layer should be no more than about $\frac{1}{10}$ of the development voltage. Generally, the resistivity of the conductive layer should be less than about 10^{10} ohm-cm., depending upon processing conditions, and thickness of the layer. It is important that no air gap exists between the conductive layer and the dielectric layer in order to avoid introduction of non-uniformities in the image developed on the image layer. Exemplary conductive materials for the conductive layer include conductive paper, paper-metal foil laminates and foils, coatings or other forms of metals such as copper, iron, silver, and aluminum. The conductive layer may be in the form of a plurality of plies of conductive material or a single layer made from a single material or a mixture of materials. The conductive layer may or may not be continuous. Exemplary of a discontinuous conductive layer would be a layer of fine, closely spaced conductive dots or stripes each separated from the others.

The thickness of the field electrode sheet or the layers making up the field electrode depends to some extent upon the electrical characteristics required and upon the use of the electrode, e.g., whether it is to be a master plate for reproductions or whether it is to be a print for direct use. Generally, an opaque white field electrode sheet having an over-all thickness of as little as slightly greater than 2 microns (the dielectric layer itself being at least 2 microns) up to about 50 mils is most suitable.

The electrical potential applied between the field electrode and the developer applicator roller surface or between the field electrode and transfer sheet (when the field electrode is employed as an intermediate) is obtained from conventional sources such as batteries or rectifiers, etc. and should be of direct current potential. A pulsating direct current may be employed preferably in the range of 1 to 10 kc. per second. The required electrical potential varies over a wide range of about 10 to about 5000 volts or higher, sufficient to provide an effective electrical field at the surface of the differentially conductive pattern but below that voltage which would cause a corona discharge between the applicator and the field electrode surface. Preferably about 500 to about 4000 volts are utilized.

After the differentially conductive pattern on the field electrode has been developed, the developer powder may be fixed by conventional techniques to the field electrode to make the pattern permanent or it may be transferred to another sheet and then fixed.

In order not to unduly lengthen the description of this invention, the following commonly assigned applications are referred to for the indicated disclosure which is relevant but not essential to a full and complete description and understanding of the present invention: U.S. Ser. No. 663,818 (elaboration of electrographic process employing field electrode of this invention both for use as a direct copy and as an intermediate); U.S. Ser. No. 640,720, now U.S. Pat. No. 3,455,276 (details of a conductive developer powder applicator for use in conjunction with the field electrode of this invention); and U.S. Ser. No. 746,691, now U.S. Pat. No. 3,639,245 (details of a suitable conductive developer powder for use in conjunction with the field electrode of this invention).

The following non-limiting examples are provided in which all parts and percentages are by weight unless otherwise stated. The reproduction steps are understood to be carried out in the absence of extraneous light.

EXAMPLE I

A dispersion of 44 parts by weight of photoconductive French process zinc oxide powder, 36 parts by weight of 30% by weight of a styrene-butadiene resin (sold under the trade name Pliolite S-7) in toluene, 30 parts by weight of acetone, and 4×10^{-4} grams of Phosphine R (C.I. 75

46055) per gram of zinc oxide as a 2% by weight alcohol solution is ballmilled for 12 hours. The dispersion is coated 4 mils thick (wet) on a one mil polyester (Mylar) film, the back of which has been vapor coated with a continuous opaque aluminum layer (resistance of 10 ohms per square) and dried at room temperature with a subsequent dark adapting period of 12 hours at room temperature. The process of dark adapting can be accelerated by increasing the temperature to 100° C. This field electrode is exposed to a projected positive image with 10 foot-candles falling on the photoconductive surface for one second. The transverse dark resistance for a one square centimeter surface area of photoconductive layer is 1×10^8 ohms and the resistance in the light exposed areas is 1×10^4 ohms for one square centimeter of surface area. This corresponds to a resistivity of approximately 5×10^{10} ohm-cm. in dark areas and 5×10^6 ohm-cm. in light exposed areas.

To develop the electrode, a potential of about +1500 volts is applied to a conductive-magnetic development roll as described in commonly assigned application Ser. No. 640,720. The development roll supplies a conductive developer powder as described in commonly assigned application Ser. No. 746,691. The field electrode moves past the development roll at a rate of 10 inches per second. The conductive layer of the field electrode is grounded during this operation. The developed sheet is removed and the image fused with an infrared lamp. The image quality is excellent and the background level is very low. This field electrode can be processed over a wide range of surface speeds, for example, from less than 1 inch per second to more than 100 inches per second. A voltage increase is required for higher processing speeds.

The following layers are substituted for the 1 mil polyester (Mylar) film: 1 mil polypropylene, 2 mil polyethylene, 2 mil polystyrene, 3 mil polyester, 0.5 mil polyester, 5 mil polyester, and 0.25 mil polyester. Each of these layers is vapor coated with an opaque conductive layer of aluminum (resistance less than about 10 ohms per square). The thickness of the dielectric layer determines the voltage to be applied for a given photoconductive layer. Each of these constructions results in a good copy. The operation of these layers is not restricted by moisture content of the ambient air. The reproducibility and control is excellent with this type of construction. The conductive back layer assures reproducibility, uniformity, and the ability to remove the field electrode from a conductive support. Absent an integral conductive layer, separation of the independent associated conductive layer from the remainder of the field electrode bearing the developed image results in drastic rearrangement of the charges with consequent disturbing of the image. If the above layer is coated on aluminum foil without a dielectric layer, the image density is less and the photoconductive layer tends to short out with resultant permanent damage and the inability to re-use same. The exposure required is 40 foot-candle seconds or four times that required when a dielectric layer is present and the background fog level is higher than is desirable.

EXAMPLE II

A dispersion of 44 parts by weight of photoconductive French process zinc oxide powder, 36 parts by weight of 30% by weight of a styrene-butadiene resin (sold under the trade name Pliolite S-7) in toluene, 30 parts by weight of acetone, and 4×10^{-4} grams of Setoflavine T and Rhodamine B per gram of zinc oxide as a 2% by weight alcoholic solution is ballmilled for 12 hours. The dispersion is coated 4 mils thick (wet) on a 3 mil conductive paper coated with a 0.5 mil layer of a polycarbonate resin sold under the trade name Lexan. The conductive paper base is treated with a conductive cationic resin available under the trade name Calgon 261. Conductivity of the paper base is more than 10^{-7} ohm $^{-1}$ -cm. $^{-1}$ over the humidity range tested. The coating is dried at room temperature with a subsequent dark adapting period of 12 hours. The resulting field electrode is exposed to a projected positive

11

image with 10 foot-candles falling on the photoconductive surface for one second. The transverse dark resistance for a one square centimeter surface area of photoconductive layer is 5×10^8 ohms and the resistance in the light exposed areas is 1×10^4 ohms for one square centimeter of surface area. This corresponds to a resistivity of approximately 2.5×10^{11} ohm-cm. in dark areas and 5×10^6 ohm-cm. in light exposed areas. The sheet is developed with a potential of +2000 volts as described in Example 1. The resultant quality in terms of resolution, image density and fog level is essentially equal to that of Example 1.

The polycarbonate resin can be substituted with polystyrene resin, cellulose acetate propionate resin, methyl methacrylate resin, polyvinylchloride resin and polyethylene resin with similar results. Employing a dielectric having a thickness less than 0.1 mil or 2.0 microns results in electrical breakdown and high copy background at the development voltages employed. Coating the dispersion directly on the conductive paper backing results in poor resolution, electrical breakdown, low image density, and high background. The above conducting backing can be replaced with others, for example, papers which are loaded with conductive fibers or other humectants. If the photoconductor is coated directly on a conductive paper backing such as is found in papers for conventional electrostatic electrophotography, then the background can easily reach 0.3 reflected optical density units above the sheet color of an unexposed and unprocessed sheet and the required exposure of the coating is large, resulting in an unacceptable copy.

EXAMPLE III

A dispersion of 38 parts by weight of photosensitive titanium dioxide (rutile) powder, 16 parts by weight of Pliolite S-7 (30% by weight) in toluene, 3 parts by weight of polystyrene, 40 parts by weight toluene and 1×10^{-4} grams of Phosphine R per gram of titanium dioxide as a 2% by weight alcoholic solution is ballmilled for 12 hours. The dispersion is coated 2 mils thick (wet) on 1 mil polyester (Mylar) film, the back of which is vapor coated with a continuous copper layer and dried at room temperature. All coating operations are done under safelight conditions. This field electrode is exposed to a positive image pattern by reflex optics in accordance with commonly assigned application Ser. No. 640,457, now abandoned. The exposed field electrode is processed on a rotating drum at 20 inches per second surface speed. The image is transferred to paper on each cycle. The development voltage is +1200 volts and the transfer voltage is -500 volts, both voltages with respect to the grounded conductive layer. Twenty copies are made from one exposure. The apparatus for processing this field electrode is described in application Ser. No. 640,547. The field electrode can be dark adapted and re-used for a new exposure. The density range of the graphic original was from 0.2 to 1.5 reflected optical density units. This total original input density can be reproduced with an effective gamma of 2.0. If this photosensitive layer is coated directly on a conductive substrate, then the image density is low, electrical breakdown results (spots or defects) and one can only faithfully reproduce part of the above input densities. More rapid decay of the photosensitive memory effect also occurs without the dielectric layer and fewer copies can be made from one exposure. This total construction (dielectric layer present) yields good copies insensitive to changes in relative humidity unlike the case with normal paper backings.

EXAMPLE IV

The surface of a 2 mil polyester film, the back of which is coated with a 70% transmission chromium layer, is dip coated with a 4% by weight of water-alcohol dispersion of Baymal (colloidal alumina) and dried. The transparent sheet is passed through a commercial infrared copy-

12

ing machine in contact with an original. The heat pattern effectively decreases the surface conductivity of the hydrophilic Baymal layer. A hot stylus will also provide the source of heat for an image pattern. The transparency is developed as described in Example I at the rate of 10 inches per second at a development voltage of +2000 volts with respect to the conductive chromium layer. The developed image may be fused or the sheet may be used as a master for multiple copies and processed as per Example III.

Other methods of creating differential conductivity patterns by heat will also work to produce a field electrode for the present process. For example, layers which strongly supercool and contain an ionic material such as diphenylphthalate containing lithium salts will give a differential conductivity pattern. Heat sensitive reactants in which a metallic species is produced is another example of such a system as well as a light activated silver halide system.

EXAMPLE V

This example is similar to Example I except that a permanent image pattern results after a first development. After exposing a zinc oxide field electrode, made in accordance with Example I, to a projected positive image, the field electrode is developed as described in Example I except that a special developer powder is used which renders the zinc oxide permanently relatively insulating and nonphotoconductive in those areas where the powder is deposited during the first development. Material such as peroxides and primary amines destroy the photoconductive response of some photoconductors such as zinc oxide. The use of such materials as the developer powder will produce the permanent relatively insulating, nonphotoconductive image pattern when developed in accordance with Example I. This resulting permanent image pattern can then subsequently be developed with any suitable powder at any later time by a uniform exposure of the entire field electrode to light and then proceeding with the development and transfer of powder images as in Example III. The uniform exposure of the entire field electrode is to render the areas where no deactivating powder was deposited conductive again in the event their photoconductivity had decayed. This uniform exposure should be roughly equivalent to the exposure required to get no developer powder deposition in those still-activated areas which is about 10 foot-candle seconds for this material. If the photoconductivity of these areas has not completely decayed just prior to a subsequent development cycle, then the uniform exposure need only restore the still-activated areas to their original conductivity, which may not require the full original exposure of 10 foot-candle seconds. However, it would not be unduly damaging to the copy quality if too much exposure were used for the uniform exposure. The deactivating material may also be applied by a stencil, painting, or may be created by a photochemical or thermal decomposition reaction in lieu of the imagewise exposure and first development step. This type of procedure is especially useful for preparing a master for multiple copies.

EXAMPLE VI

To compare the developed images with and without the dielectric layer between the image layer and the conductive layer, identical coatings of TiO_2 -10% by weight ZnO in a styrene-butadiene copolymer binder were applied to both the aluminum vapor coated side of 1 mil polyester film and to the side away from the aluminum vapor coated side of 1 mil polyester film. The aluminum vapor coat was at least 250 angstroms thick and the image layer was exposed to a light image by exposing it through a transparency of the USAF 1951 Resolving Power Test Target in contact with it. A gray scale was also attached to the test target. The exposure was from a tungsten incandescent lamp some distance from the copy plane, and the light intensity measured at the copy plane was 20 foot-

candles as measured by a standard light meter. Exposure was for 1 second, giving a 20 foot-candle second exposure, unless otherwise specified.

The exposed field electrodes were developed on a rotating electronically conductive drum moving at a surface speed of 22.4 cm./sec. past a rotating conductive magnetic development roller as described in U.S. application Ser. No. 663,818, now U.S. Pat. No. 3,563,134. The gap between the development roller and the top surface of the field electrode (the surface of the image layer) was maintained at 15 mils. A series of development voltages were run for both types of field electrode construction with and without a dielectric layer. In all cases, the powdered development roller was positive with respect to the conductive drum, and the conductive layer of the field electrode was electrically connected to the conductive drum. The developer powder composition was the following in parts by weight: 40—Epon 1004 (trade name for an epoxy resin); 60—Magnetite; 0.8—carbon black; and 0.1 Cab-O-Sil M5 (trade name for finely divided silica).

After the field electrode was developed, it was carefully removed from the drum and the powder fused by contact with a heating blanket at 125–150° C. for 5–10 seconds.

The field electrodes were then compared for background optical density, maximum optical density in black areas, over-all best compromise, and processing latitude (non-criticality in development voltages, etc.). The reflection optical densities were measured in the conventional manner in accordance with the specifications given in American Standard-Visual Diffuse Reflection Density, PH2.17—1958. A Macbeth Model RD-100 Reflection Densitometer with a Wratten No. 25 red filter was used. The filter minimizes the effect of the pink color of the dye sensitized photoconductive layer.

The results are given in the tabel below wherein D_{max} refers to the optical density of the large black square of the test target, and D_{bknd} refers to the background optical density. The optical density of an unexposed, unprocessed sheet is approximately 0.12. Contrast is here given as $(D_{max} - D_{bknd})$. All optical densities given are the average of 4 readings.

TABLE I

	No intermediate dielectric layer	Intermediate dielectric layer
1. Low background optical density sought:		
D_{max}	0.54	1.10
D_{bknd}	0.18	.13
Contrast.....	.36	.97
2. Highest optical density in black area sought:		
D_{max}	1.10	1.24
D_{bknd}	0.56	0.14
Contrast.....	.54	1.10
3. Overall best compromise copy sought:		
D_{max}	0.83	1.24
D_{bknd}	0.20	0.14
Contrast.....	.63	1.10
4. Useful processing voltage range.....	(1)	(2)

¹ Very narrow range, essentially (100 v. to 300 v., but best is not as good as those at right).

² Good copies over considerable range (300 v. to 2,000 v. give good copies).

In the case of the over-all best compromise copy, the exposures were allowed to be different to get the best copy. The exposure for the case of an intermediate dielectric layer was still 20 foot-candle seconds and uncritical. The exposure for the case of no intermediate dielectric layer was 40 foot-candle seconds.

The dielectric layer as defined herein eliminates the disparity in charge flow between conductive and non-conductive regions and thus reduces the quantity of developer powder deposited in the background areas as a result of the direct dependency upon charge flow. Significantly, the desirability of this dielectric layer in a field electrode designed for use in a dynamic electrographic process as herein described would be detrimental in conventional electro-

static duplicating processes. This is the case because in electrostatic processes dielectric layers of the thickness herein contemplated would prevent intermingling of electrostatic charges between the photoconductive and conductive layers in the illuminated areas, this thereby reducing the degree of difference in surface potential between light and non-light struck areas. See Dessauer, U.S. Pat. No. 2,901,348, especially the disclosure regarding barrier layer 12. In such electrostatic processes, it is this difference in surface potential which gives rise to a differential field and attracts electroscopic toner powder in the development stage. Dielectric layers which are very thin (2 microns or less) or breakdown or otherwise transport charge under the electrical fields which build up across it may be tolerated in such electrostatic processes but in those cases, the dielectric layer is not functioning as a true blocking layer to shut off charge flow.

What is claimed is:

1. An electrographic field electrode developable by conductive particulate under a development voltage comprising an image layer located on one surface of said field electrode adapted to provide a differentially electronically conductive image pattern in the form of relative conductive and non-conductive regions, a dielectric layer bonded to said image layer, said dielectric layer having a thickness of at least 6 microns and a resistivity of at least about 10^{11} ohm-cm. and being adapted to equalize the charge flow through said conductive and non-conductive regions of said image layer, and a conductive layer bonded to said dielectric layer, said conductive layer having a conductivity such that substantially no voltage drop occurs under said development voltage, said dielectric layer having a conductivity of no more than .1 the conductivity of said conductive layer and .1 the conductivity of said conductive regions of said image layer.

2. The field electrode of claim 1 wherein said image layer is photosensitive.

3. The field electrode of claim 1 wherein said image layer is photoconductive.

4. The field electrode of claim 1 wherein said image layer comprises an inorganic photoconductor disposed in an insulating binder.

5. The field electrode of claim 1 wherein said image layer comprises photoconductive zinc oxide disposed in an insulating binder.

6. The field electrode of claim 1 wherein said image layer comprises photoconductive titanium dioxide disposed in an insulating binder.

7. The field electrode of claim 1 wherein said dielectric layer has a thickness of at least 13 microns and said image layer is adapted to provide relative conductive regions which are at least about twice as conductive as said non-conductive regions.

8. The field electrode of claim 1 wherein said dielectric layer is an organic polymeric film.

9. The field electrode of claim 1 wherein said dielectric layer is a polyester film.

10. The field electrode of claim 1 wherein said conductive layer has a transverse resistivity of less than about 10^{10} ohm-cm.

11. The field electrode of claim 1 wherein said conductive layer is a metal film.

12. The field electrode of claim 1 wherein said conductive layer is a vapor coated metal film.

13. The field electrode of claim 1 wherein said conductive layer is a vapor coated film of aluminum.

14. An electrographic process comprising (1) providing an image pattern defined by relatively conductive and non-conductive regions on at least the surface of an image layer of a field electrode, said field electrode comprising said image layer located on one surface of said field electrode adapted to provide a differentially electronically conductive image pattern in the form of relative conductive and non-conductive regions, a dielectric layer bonded to said image layer, said dielectric layer being of a thick-

15

ness and resistivity adapted to allow only a predetermined amount of electrical charge to pass in each unit area of said image layer under said development voltage, and a conductive layer bonded to said dielectric layer, said conductive layer having a conductivity such that substantially no voltage drop occurs under said development voltage, (2) contacting a unit area of said image pattern with an electrically conductive applicator surface bearing a uniform layer of electrically conductive developer material, said developer material being held on said applicator surface by a first force, (3) concurrently with said contact imposing a direct current electrical potential between said conductive layer and said electrically conductive applicator surface in said unit area to create a transient potential difference in said unit area between said developer material and said relatively non-conductive regions, (4) maintaining said contact for a period sufficient to permit said transient potential difference to assume a level where it exerts a transfer force greater than said first force holding said developer material on said electrically conductive applicator surface, and (5) breaking the contact between said applicator surface and said image layer in said unit area while said electrical potential is maintained and said transfer force exerted by said transient potential difference in said relatively non-conducting regions is greater than said applicator force, whereby said developer material transfers to the surface of said image layers in said relatively non-conductive regions within said unit

16

area, and repeating steps (2)-(5) until the aggregate of unit areas includes all of said image layer desired to be developed.

15. The field electrode of claim 1 wherein said dielectric layer is at least 10 microns thick.

16. The field electrode of claim 1 wherein said image layer is photoconductive, said dielectric layer is at least 13 microns thick, and said conductive layer is a metal.

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U.S. Cl. X.R.

96—1.8, 27; 117—215, 218

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,764,313

Dated October 9, 1973

Inventor(s) Benjamin L. Shely

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 9, line 49, change "mak" to --make--.

Column 10, line 3, change "mols" to --mils--.

Column 11, line 46, change "640,457" to --640,547--.

Signed and sealed this 9th day of July 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents