Feb. 16, 1971 **B. L. SHELY** 3,563,734

ELECTROGRAPHIC PROCESS

Filed Aug. 28, 1967 2 Sheets-Sheet 1

FIG. 1

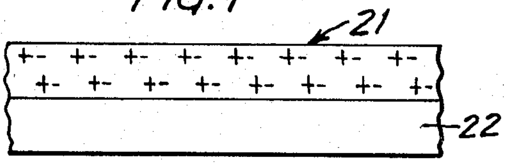

FIG. 2

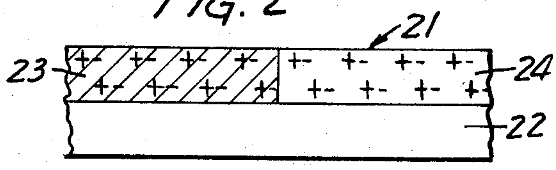

FIG. 3

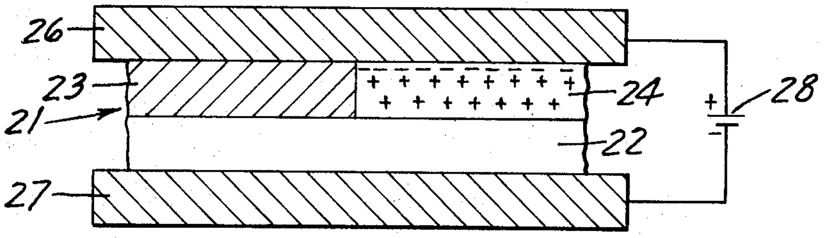

FIG. 4a

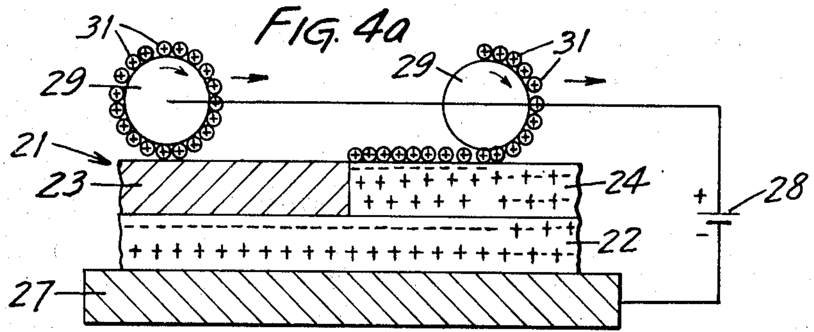

FIG. 4b

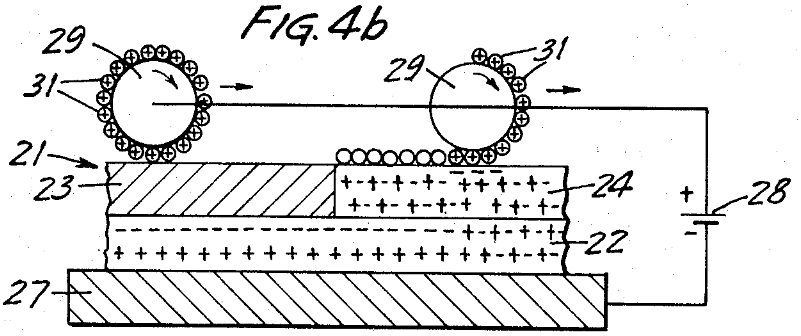

FIG. 5

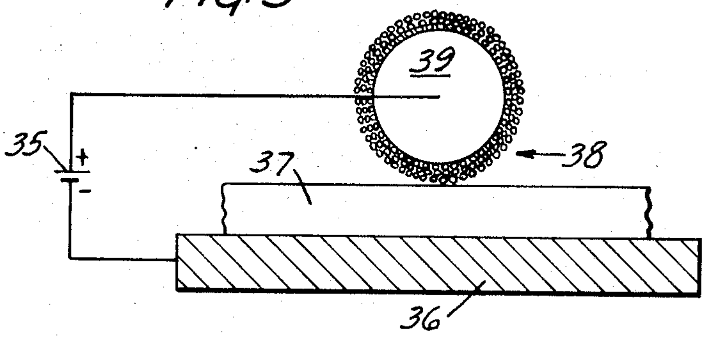

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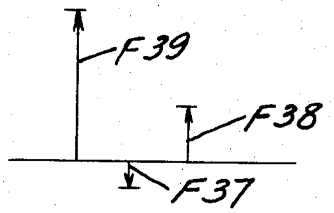
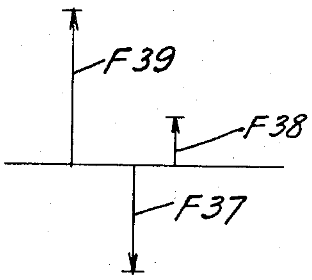
FIG. 6



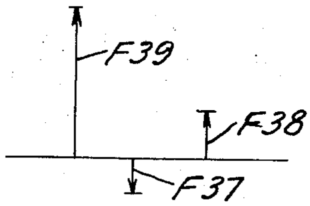
NO APPLIED FIELD

FIG. 7



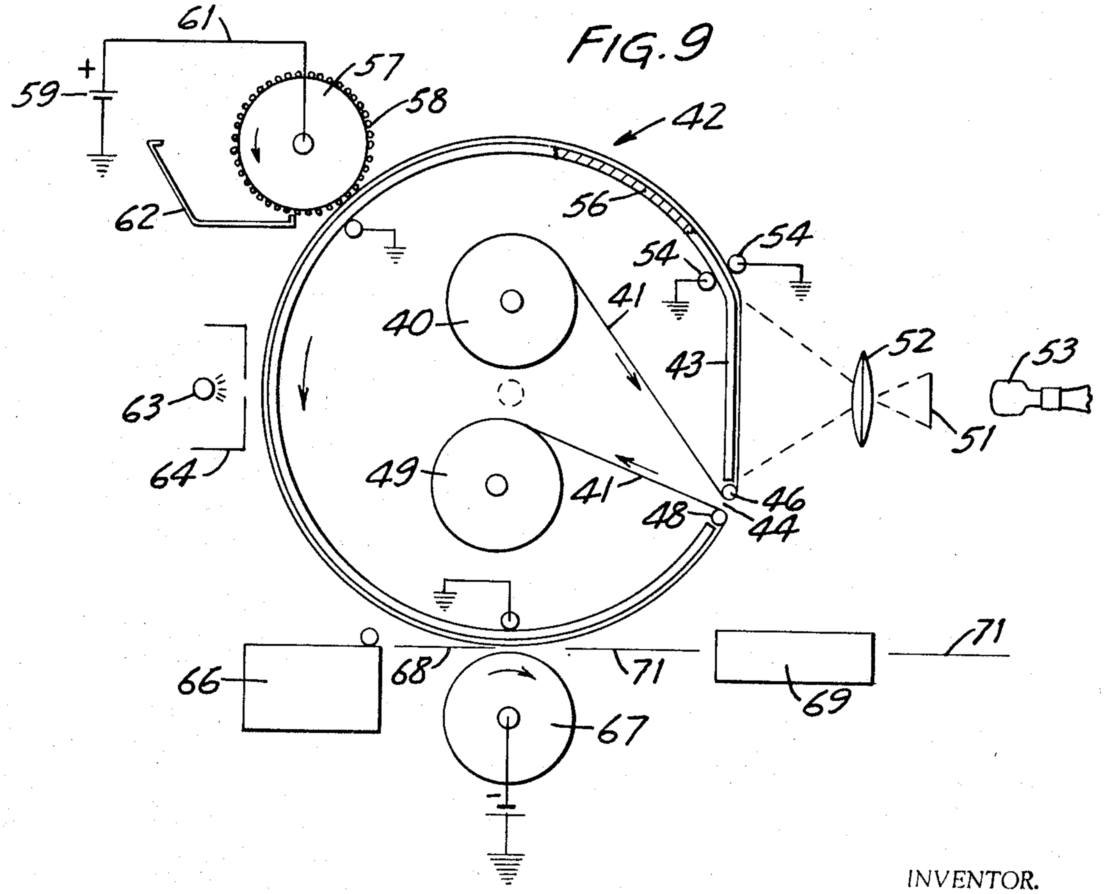
APPLIED FIELD
(NON CONDUCTIVE AREA)

FIG. 8



APPLIED FIELD
(CONDUCTIVE AREA)

FIG. 9



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ELECTROGRAPHIC PROCESS

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Continuation-in-part of applications Ser. No. 403,737, Oct. 14, 1964, and Ser. No. 567,170, July 22, 1966. This application Aug. 28, 1967, Ser. No. 663,818

Int. Cl. G03g *13/08, 13/16, 13/22, 15/08*

U.S. Cl. 96—1.4 16 Claims

ABSTRACT OF THE DISCLOSURE

An exposed photoconductive sheet is contacted with conductive developer powder applied from a conductive surface to which it is adhered while creating a differential electrical field between the photoconductive sheet and the conductive surface containing the adhered developer powder such that developer powder is transferred selectively to the photoconductive sheet in the nonexposed areas and separation of the photoconductive sheet from the source of supply of developer powder is made while still maintainting the influence of the electrical field and provision is made for continuing the attraction of the developer powder to the surface of the photoconductive sheet after the aforesaid separation.

This application 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 present invention relates to a novel and useful reproduction system. In one aspect this invention relates to the permanent reproduction of images or graphic intelligence on a surface. In another aspect this invention relates to the reproduction of an image by a photoelectric technique.

The use of electrosensitive receptors as a means for reproducing images and patterns and recording graphic intelligence has been known for some time. There are many variations of such electrographic techniques including the so-called electrostatic process and the electrolytic process. These electrographic processes use a photoconductive surface on a suitable receptor which is rendered transversely differentially conductive, such as by irradiation. In the electrostatic process, an electrostatic charge pattern is obtained by electrostatically charging a photoconductive sheet, then producing a transversely differentially conductive pattern by exposing the photoconductive sheet to a light image or light pattern. The electrostatic charge pattern thus created is then developed by attracting a highly resistant developer powder to the surface in a pattern corresponding to the image. In the electrolytic process, a transversely differentially conductive pattern on the photoconductive sheet is utilized as an electrode in an electrolytic cell. Development is achieved by electrolytically (ironically) de-positing a developer material on the conductive portions of the receptor sheet. There also have been suggestions of using liquid in a capillary such as a sponge wherein the application of an electrostatic charge to a surface draws the liquid through the capillary to the surface for marking. Still another process contacts the exposed photoconductive sheet with conductive developer powder during the application of a differential electrical field. These processes involve several steps for obtaining the differentially conductive pattern and the development of the image. Each has its inherent limitations as to cost, quality, reliability, operation and form of image reproduced, i.e. negative or positive. It is the purpose of this invention to provide a simple, flexible and high quality, reliable process for reproduction of an image or graphic intelligence.

The present versatile process has the capability of delivering a positive or negative copy of a light pattern in good quality. The process is as sensitive and in some respects more sensitive than conventional electrophotography, particularly the electrolytic process, for a given sensitized photoconductive composition.

Various objects and advantages will become apparent to those skilled in the art from the accompanying description and disclosure.

According to this invention, a differentially electronically conductive pattern corresponding to the graphic intelligence to be reproduced is created transversely through or longitudinally on an insulating layer electrode (field electrode), such as by exposure of a dark adapted photoconductive sheet to a light image in the absence of extraneous light. While the differentially conductive pattern is present, the entire field electrode surface is uniformly contacted with a developer or marking material, for example, by means of an electronically conductive roller or cylinder having adhered to the outside surface thereof a layer of electronically conductive developer powder. Concurrently with the application of the developer powder to the field electrode surface, an electrical field is created by applying a direct current electrical potential between the field electrode containing the differentially conductive pattern and the applicator of the developer material. An electronically conductive path is created between the differentially conductive pattern of the field electrode and the applicator, such as through the circuit made by an electronically conductive powder developer material. This conductive path is not ionic as in the case of the electrolytic process. Separation of the developer applicator from the field electrode surface at the end of the development stage must be made while the electrical field is still maintained. The developer or marking material selectively deposits on the electrode surface in a patternwise manner. In normal operation, a visible reproduction of the differentially conductive pattern and thus of the graphic intelligence is obtained by deposition of the developer in the relatively nonconductive areas of the differentially conductive pattern of the surface of the field electrode. However, if the field electrode is a rectifier in the conductive areas to the direction of current being passed, a visible reproduction corresponding to the graphic intelligence is produced by deposition of developer in the relatively conductive areas of the differentially conductive pattern on the surface of the field electrode. Thus, when the field electrode is an exposed N-type photoconductive sheet and is the anode, the developer is deposited on the relatively conductive areas (light exposed areas). Similarly when the field electrode is an exposed P-type photoconductive sheet and is the cathode, developer is deposited on the relatively conductive areas (light exposed areas). Otherwise when the current is passing in the normal direction characteristic of the particular type of semiconductor, deposition of developer is in the relatively nonconductive areas.

No electrostatic precharging of the field electrode surface is required nor is it desirable because for one reason it adds another step to the process and also requires special considerations in the construction of the field electrode. The creation of the differentially conductive pattern and the development step may be carried out simultaneously or development may follow the creation of the conductive pattern when the pattern has a finite permanence.

The field electrode surface may be the final reproduction of the pattern or other graphic intelligence or may serve as an intermediate or master for subsequent use in reproducing the image or pattern on ordinary paper or other suitable transfer surface. In either case, upon separation and removal of the field electrode from the development step provision is made for at least temporarily adhering the developer material to the surface of the field electrode to assure retention of the developed image thereon until further treatment or transfer. If the field electrode is to be the final reproduction, usually the developed image constituting the developer material held to the surface is fixed by chemical or physical methods. For example, developer powder may contain a low melting resin on the surface or in the core of the particles which when heated will fuse the particles of developer to the electrode surface.

When the differentially conductive pattern of the field electrode still remains or is regenerated after development, the field electrode may be used as a master for making further copies. Thus, when the electrode surface is to act as a master for a subsequent copy there is no fixing of the developed image thereon but the image is transferred to a suitable transfer sheet conveniently by passing the insulating layer or field electrode face to face with the transfer sheet through the nip region of two conductive rollers which press the surfaces of the two sheets together while simultaneously applying an electrical potential (preferably of reverse polarity with respect to the developing potential) between the conductive rollers in a manner and under conditions similar to that used in the development of the image on the field electrode. In this manner the image on the electrode surface is transferred to the transfer sheet when the sheet is separated from the electrode surface; the transfer sheet is then treated to fix the image thereon as indicated above. When the field electrode is a photoconductive sheet and the sheet is exposed to a light image and developed in the dark, transfer of the image from the surface of the field electrode to the transfer sheet is facilitated if the surface of the electrode containing the developed image is uniformly light exposed before the transfer process so that the nondeveloped areas are reexposed to light. (The developed areas are not light struck because of the opaqueness of the developer.) Also in the case of a photoconductive field electrode, it may be reused for a new pattern by suitable cleaning and dark adapting.

When it is desired to make more than one copy of the graphic intelligence represented by the differentially conductive pattern of the field electrode, instead of reusing the field electrode surface for a new pattern, the field electrode is again coated with the developer while applying the unidirectional electrical potential in a manner as described above and the developed pattern on the surface of the field electrode is transferred to another transfer sheet as before. This cycle of development of the field electrode and transfer of the resulting developed image may be repeated as long as the differentially conductive pattern of the field electrode persists. This cycle of development and transfer of the entire pattern usually takes no longer than a fraction of a second. Thus even with a transient conductive pattern as exists with many photoconductors, 20 to 100 copies or more may be made with a photoconductive field electrode. Exposing the developed photoconductive electrode surface to light between the development step and the transfer step increases the number of copies that can be obtained.

Since the differentially electronically conductive pattern of the insulating field electrode is an essential part of the present invention, at this point the operation of the invention in relation to such pattern will be described. Reference will be made to FIGS. 1 through 4 which diagrammatically show, by elevational views, the various steps of creating the electronically conductive pattern, application of the electrical field and the developement of the electronically conductive pattern with the developer during the application of the field.

FIG. 1 is a diagrammatic illustration in cross section of a suitable field electrode having an insulating surface layer **21** of material which contains charge carriers on a suitable support or backing **22**. The free charges are designated by (+) and (−). FIG. 2 shows diagrammatically the same layer **21** in which the left side **23** is made transversely relatively conductive and the right side **24** remains insulating. In FIG. 3, layer **21** and its support **22** of FIG. 2 are placed between and in contact with two conductive plates **26** and **27**. A unidirectional electrical potential from conventional source **28** is applied as shown to form an effective electrical field across the interface of layer **21** and plate **26**, the anode contact being made with the differentially conductive surface of layer **21**. In the conductive area **23** of FIG. 3, the negative charges are extracted by the conductive plate **26** as the result of the electronically conductive path through conductive area **23** to plate **26** whereas in the nonconductive area **24** the negative charges cannot be extracted and instead they segregate and remain at the surface of layer **21** as shown as long as the electrical potential is maintained, the negative charges being adjacent to anode **26** and the positive charges being adjacent to cathode **27**. The insulating properties of nonconductive area **24** of FIG. 3 prevent the charges from being extracted onto the conductive plates because there is no conductive path. The same phenomena is observed when the only change in conductance of layer **21** is on the surface itself. In other words, there may be no observable change in the transverse conductance or resistance but the surface (longitudinal) conductance of the surface areas **23** and **24** differ, i.e. the surface of area **23** being made conductive. The charges in area **23** at this surface accumulate adjacent to the interface and are extracted onto plate **26** as the result of the conductive path between the surface of area **23** and plate **26** although the movement of the charges in the interior are not as great as in the case where there is transverse conductance. In still another modification, the surface resistance may not change and the differentially conductive pattern exists only transversely through the field electrode. In this case the electrical field breaks the surface resistance barrier in the transversely conductive areas allowing extraction of accumulated charges adjacent the surface.

In case backing layer **22** is highly resistive, a resistivity of 10^{12} ohms per centimeter or more such as obtained with a Mylar film, the charge distribution in the nonconductive portion **24** of layer **21** remains even after discontinuance of the electrical potential from source **28**. Eventually, however, the charge distribution will return to the prepotential (normal) situation as shown in FIG. 2, usually in about one minute or less. Where backing layer **22** is relatively conductive, such as a paper or metal backing, the charge distribution returns to normal as shown in FIG. 2 immediately upon discontinuance of the electrical potential from source **28**. This retention of the charge distribution when using a highly insulating backing **22** is due to the fact that a charge distribution is set up in the insulating backing **22** similar to that in nonconductive portion **24** of layer **21** and in itself acts as an electrical field tending to attract and repel charges in layer **21**. Due to the low mobility of the charges in such a highly insulative layer **22**, redistribution of the charges to the normal situation after discontinuance of the electrical potential is very slow.

In FIG. *4a*, plate **26** of FIG. 3 has been replaced by an electronically conductive roller **29** having on its surface a developer powder **31** and backing layer **22** is a highly insulative material such as Mylar. Developer powder **31** in FIG. *4a* is of the type having an electronically conductive surface and a highly resistive core. Roller **29** passes across the surface **21** so that powder **31** contacts the entire surface **21**. Typical positions of conductive roller **29** are shown as it progresses across the surface of insulating layer **21** in the direction shown. The conductive roller is attached to a source **28** of an electrical potential as in FIG. 3. At each position of conductive roller

29, there is shown the relationship of the charges in conductive area 23 and in the nonconductive area 24 of the insulating layer 21 and the resulting deposition of the conductive particles 31 on surface 21. The electrical field created by the electrical potential acts upon the conductive powder and the insulating layer 21 initially at the point of initial contact of powder 29 with insulating layer 21. After this initial contact and the roller moves on, the electrical field persists between powder 29 and layer 21 for reasons discussed above which persisting electrical field holds the powder 29 in place by the force of attraction due to the electrical field so that the developed surface can be moved and handled for subsequent operations, such as fixing, or transfer of the developed pattern to another surface. As is seen from FIG. 4*a*, no powder is deposited in the conductive area and powder is deposited only in the relatively nonconductive area. It appears that powder attains a positive charge and is attracted to the nonconductive area by the negative charges accumulated in the nonconductive portion adjacent the surface. In the conductive areas negative charges are not trapped.

In FIG. 4*b*, plate 26 of FIG. 3 has been replaced by an electroncially conductive roller 29 having adhered to its surface electroncially conductive developer powder 31, such as finely divided metal. In this embodiment, backing layer 22 is relatively conductive, such as is obtained with a metal layer or paper. Roller 29 passes across the surface 21 so that powder 31 contacts the entire surface 21. Typical positions of conductive roller 29 are shown as it progresses across the surface of insulating layer 21. The conductive roller is attached to a source 28 of an electrical potential as in FIG. 3. At each position of conductive roller 29, there is shown the relationship of the charges in conductive area 23 and in the nonconductive area 24 of the insulating layer 21 and the resulting deposition of the conductive particles 31 on surface 21. The electrical field acts upon the conductive powder and the insulating layer 21 only at the point of contact of the powder 29 with the insulating layer 21. Before and after this contact no electrical field influence on the insulating sheet 21 is observed and the powder 29 is held in place solely by the force of gravity. As is seen from FIG. 4*b*, no powder is deposited in the conductive pattern have a maximum transverse resistance ly nonconductive area. No charges are trapped even in the nonconductive areas after the roller applicator has passed and the deposited powder is not charged.

For the proper operation of the differentially electronically ccnductive pattern the conductive areas must be at least twice as conductive as the nonconductive areas, preferably at least 10 times as conductive. This is the case regardless of whether one considers transverse conductance or surface conductance. In the case of the use of a differentially electronically conductive pattern involving a change in surface or longitudinal conductance, the relatively conductive areas of the insulating sheet electrode (field electrode) containing the conductive pattern should have a maximum surface resistance (threshold conductance) of about 10^{10} ohms per square and the relatively nonconductive areas have a minimum surface resistance of about 10^6 ohms per square. In the case of the use of a pattern involving a change in transverse conductance, the relatively conductive areas of the insulating sheet electrode (field electrode) containing a conductive pattern have a maximum transverse resistance (threshold conductance) of about 10^8 ohms for one square centimeter under the conditions of development of the pattern (application of developer powder) and the relatively nonconductive areas have a minimum transverse resistance of about 10^4 ohms for one square centimeter. The resistance values above are those measured under a potential and for an applied time corresponding to that to be used in the process, and it is to be remembered that the conductive areas are at least twice as conductive as the nonconductive areas within the above overall ranges.

For best results, the limits of transverse resistance of both the nonconductive areas and the conductive areas of the electrode including any layer situated over the conductive pattern are between about 10^4 ohms for one square centimeter and about 10^9 ohms for one square centimeter measured at a potential corresponding to the applied potential to be used in the process. Any material or layer situated between the differentially conductive pattern layer and the developer powder should have approximately the same resistance, both transverse and surface resistance, as the relatively nonconductive areas of the differentially conductive pattern.

The differentially electronically conductive pattern of the insulating field electrode may be an integral part of an insulating sheet, or it may be a separate device such as a differentially conductive pattern in a backing plate or support for an insulating sheet, and is in the form of certain areas or lines which are relatively electronically conductive with respect to other relatively nonconductive areas or lines.

The differentially electronically conductive pattern may be obtained by various methods such as by the use of a semiconductive layer or a photoconductive layer, and such methods will be hereinafter discussed more fully in connection with the characteristics and construction of specific field electrodes. In the use of a photoconductive layer on an insulating sheet to create the differentially conductive pattern, the resistance hereinbefore discussed 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. The insulating field electrode contains a metal layer integral therewith or a separate metal backing plate, for electrical connection of the electrical potential source to the aforesaid differentially conductive pattern.

The developer is an important aspect of the present invention since it is the marking material and also an integral part of the electrical circuit. This developer is usually a finely divided powder and colored so as to contrast with the usually white surface of the field electrode or the transfer sheet. The developer powder should be electronically conductive or at least not a good insulator, so as to minimize the resistance of the electronic circuit or path between the connections of the electrical potential to the field electrode and the developer applicator, i.e. so that substantially all of the voltage drop does not occur across the powder layer. For development purposes the developer powder should have a conductivity of at least 10^{-10} mhos per centimeter (ohms^{-1} cm.$^{-1}$), preferably 10^{-2} to 10^{-7} mhos per centimeter, at the applied field, preferably at least 1000 volts per centimeter, to be used in the circuit when the powder is compressed into 1 centimeter cube between brass electrodes fitted in a rigid chamber and conductance of the cube measured between the electrodes (static test). A pressure of 86 pounds per square inch (6.05 kg. 1 cm.^{2}) is applied before and during the measurement of conductance. Conductance is measured with conventional circuitry and conductivity is plotted as a function of the applied field in volts per centimeter. However, higher resistive (lower conductive) particles as high as 10^{14} ohms centimeter may be used where the developer powder is applied under conditions where the electrical circuit is completed by other means such as by conductive bristles or filament of a brush applicator or of a roller applicator containing a conductive flocked surface such as flocked rayon treated with an aqueous solution of a conductive metal salt, e.g. NaCl.

If the developer particles are to be used in accordance with the teachings of FIG. 4*a* or are to be transferred from the field electrode to a transfer sheet as previously mentioned for making copies, the developer particles should also have the capability of retaining their polarization imparted to them by the applied electrical field during the development of the pattern on the field electrode. To achieve this the conductive developer particle should have a highly resistive interior (a resistivity of at least 10^5 ohms centimeter at the applied field) with a highly conductive surface (surface resistance not greater than 10^{10} ohms per square at the applied field), preferably a discontinuous conductive surface. For example, a highly resistive resinous spherical core or granule with about half of its exterior surface covered with relatively smaller highly conductive particles such as carbon black or metal particles and semiconductive particles have been found very satisfactory.

Thus, the preferred developer powder for both development and transfer is one which has a relatively high conductance at least on the surface to assure rapid polarization and yet is able to retain such polarization once induced for a finite period of time, e.g. one-half second or more.

The size and shape of the developer particles are also important. When using relatively less conductive particles, best results are obtained with spherical particles. The contrast characteristics of the developed pattern can be controlled by varying the particle size and particle size distribution. The particle size is usually between about 1 and 50 microns, preferably between about 2 and about 15 or 30 microns. Such particles may be conveniently made by spray drying an organic solution or emulsion of the developer material, and subsequently classifying the particles in the desired size range. If fixing is to be done by the use of a low melting resin, the low melting resin is dissolved in the spray drying solution or emulsion and the mixture spray dried. Also a melt may be made of resin in which conductive pigment or powder is dispersed which is solidified and pulverized or a conductive pigment or powder is spread over a molten sphere of resin and then the mass solidified. The developer powder may include an inert pigment, magnetic particles, or a chemical which reacts with another chemical on the surface of the electrode or final transfer sheet. For example, the developer powder may be silver nitrate or acetate, and the surface of the transfer paper or the field electrode is treated with hydroquinone. Upon heating there is a reaction between the silver nitrate or acetate and the hydroquinone to form a black image. With reactive developer powders, no resin is necessary for fixing. When a resin is used as part of the developer powder for fixing, the ratio of developer pigment to resin is usually greater than 0.1:1, preferably between about 0.5:1 and about 2:1 by weight.

Since the invention involves attraction of the developer particles from the applicator to the surface of the field electrode or transfer sheet upon the application of a direct current electrical potential, the forces of attraction between the various surfaces and between the particles themselves are critical. Essentially there are two forces involved in the phenomena of the present invention. The first force is the attraction of the developer particles to the applicator and the second force is the attraction of the developer particles to the surface of the field electrode including both that attractive force created upon the application of an electrical potential and that attractive force remaining after discontinuance of the electrical potential. For practical purposes there is also a third force and that is the cohesive force between developer particles. Such cohesive forces between particles permits the developer particles to form multiple layers on the applicator and results in a greater density of the reproduced image or pattern. Once the materials of the system have been selected the adhesive force between the applicator and the particles and the cohesive force between the developer particles themselves are constant or fixed. On the other hand the force of attractiton of the developer particles to the field electrode is variable and depends upon the conductance of the field electrode and upon the electrical potential applied during contact between the field electrode and applicator.

When an electrical potential is applied between the applicator and the field electrode over those areas where it is not intended for the developer particles to be deposited, the adhesive force or attractive force between the developer particles and the applicator must be greater than the adhesive force between developer particles and the surface of the field electrode. Similarly the cohesive forces between the particles must be greater than the attractive force to the field electrode when a multiple layer of particles on the applicator is utilized. On the other hand, upon the application of a suitable electrical potential between the applicator and the conductive pattern in those areas to be marked, the attractive force of the particles to the field electrode must be greater than either the cohesive force between the particles or the adhesive force of the particles to the applicator. In the case of a multiple layer of particles on the applicator the attractive force to the field electrode need be only greater than the cohesive force between the particles. In the case of a single layer of developer particles on the applicator the attractive force to the field electrode must be greater than the adhesive force of the particles to the applicator. The cohesive force between the developer particles should never be greater and should be preferably less than the adhesive force or attractive force between the particles and the applicator.

As a result of the application of a suitable electrical potential to produce a differential field, the developer particles are transferred from the applicator to the field electrode in those areas where the attractive force of the particles to the field electrode is greater than the other existing forces as described above. The attractive force between the developer particles and the field electrode is primarily dependent upon voltage for a given set of conditions. As to whether the developer particles deposit upon the nonconductive areas or the conductive areas of the differentially conductive pattern of the field electrode will depend in some cases upon whether the field electrode is the cathode or the anode and upon the characteristics of the field electrode itself; however, in most situations deposition is on the nonconductive areas.

For a better understanding of the forces involved reference is made to a diagrammatic elevational view of FIG. 5 which illustrates suitable apparatus including an electrical potential source **35**, a conductive metal backing plate **36**, a field electrode **37**, multiple layers of conductive developer powder **38** and a conductive metal cylindrical applicator **39**. FIG. 6 diagrammatically illustrates in graphical form the forces existing in the illustration in FIG. 5 when no electrical field potential is applied from source **35**. In FIG. 6, F**39** is the force of attraction between the applicator and developer particle which may be attained by the adhesiveness between the surface of the applicator and developer particles. F**38** is the cohesive force between the developer particles which may be attained by cohesiveness between the surfaces of the particles, and F**37** is the attractive force between the surface of the field electrode under no electrical potential and the outer developer particle layer in contact with the surface which in the case of FIG. 5 is attained by gravity. As is seen in FIG. 6, gravitational force F**37** between the field electrode and the outer developer particle layer is less than either adhesive force F**39** or cohesive force F**38**. On the application of a sufficient electrical potential from source **35** between the backing plate **36** and applicator **39** by conventional electrical connections, the forces in the illustration in FIG. 5 existing in the nonconductive areas of a differentially conductive pattern of field electrode **37** are shown in FIG. 7. As is seen from FIG. 7, the attractive force F**37** between the nonconductive areas of the field electrode and the outer conductive particle **38** is now greater than the cohesive force F**38** between particles but not greater than attractive force F**39** between the developer powder **38** and applicator **39**. As a result one or more layers of particles **38** are attracted more strongly to the field electrode **37** than to themselves, and if the applicator **39** is removed from the nonconductive surface of field electrode **37** while the electrical potential is still maintained the developer particles **38** adhere to the surface of field electrode **37** rather than the applicator **39** and are retained in place by the remaining gravitational force F**37**. FIG. 8 shows the situation as it exists in the conductive areas of field electrode **37** and as it is seen in this situation the attractive force F**37** is still less than either forces F**38** or F**39**. In this situation the removal of the applicator **39** from the conductive surface while maintaining an electrical potential does not result in particles **38** adhering to the field electrode **39**. In the conductive areas as shown in FIG. 8, the attractive force F**37** between the field electrode and the developer particle is somewhat greater but still insufficient to maintain the particles on the surface of the field electrode **37** when the applicator **39** is removed.

When only a monolayer of developer particles **38** are used on the surface of roller applicator **39**, force F**37** must be larger than force F**39** to transfer developer in accordance with FIG. 7. Also in the case of the use of a magnetic applicator and magnetically responsive powders, the balance of forces involves primarily attractive forces F**37** and F**39**, since the cohesive force F**37** between particles is negligible.

The increase in force between the field electrode **37** and the developer particles **38** appears to be due to the fact that the developer particles **38** become polarized at the point of contact with the surface of field electrode **37** and due to the polarization of the nonconductive areas of an opposite charge in the field electrode **37** adjacent the particles **38**. This phenomena was described previously in connection with FIGS. 4*a* and 4*b*

The physical characteristics of the applicator, field electrode and the developer particles assist in controlling the forces involved. A gelatin surface of an applicator as compared with a photoconductive field electrode surface comprising a photoconductor and organic resin binder has the required force of attraction for most developer particles to maintain them on the applicator. The retention of the developer particles on the surface of the applicator can also be aided and increased by mechanical means, such as by use of a flocked surface, or by use of a mesh surface; an attractive force can also be achieved by the use of a magnetic applicator in combination with magnetic developer particles. Treating the field electrode surface, such as with a fluorochemical, is also a method for controlling these forces by decreasing the adhesion of the developer particles to the electrode surface. The cohesive forces between particles can be controlled and increased by treating the surface of the developer particles with a suitable compatible high viscosity organic liquid, such as castor oil, refined mineral oil or silicones. Bulk density measurements are a convenient method of determining the proper amount of organic treating liquid on the surface of the developer particle. The maximum amount of organic liquid is used on the particle surface which can be accommodated without decreasing the bulk density of the powder more than about 20 percent. The cohesive forces between particles can also be controlled by the use of a free flowing magnetically responsive developer powder in combination with a magnetic applicator, such as a magnetic roller or magnetic brush, which has an adjustable magnetic field.

Examples of suitable developer powders include copper, iron, aluminum, silver, zinc, black iron oxide, copper oxide, copper chloride, silver oxide, cobalt oxide, indium oxide, cadmium oxide, lead oxide, tin oxide, iron acetate (reactant), barium ferrite, carbon black or aluminized glass spheres. The above materials may be used alone or in combination with each other and other materials, such as resins, to achieve the proper conductivity, adhereability, etc. Suitable resins of sufficiently low melting point which

may be used with the above materials for fixing the developer powder to the surface by heating or for imparting the appropriate resistance to the core include polystyrene, Epon resins (epichlorohydrinphenolic condensates), polyvinyl chloride and polyvinyl butyral. Meltable organic compounds such as benzil, benzoin, paratoluensulfonamide and diphenylphthalate can also serve as binding agents for the developer powder in place of, or in addition to, the resins. The proportion of resin in the developer powder also may determine the conductivity of the powder. The above materials alone may be used without admixture with resins when the receptor contains a sticky material or when the receptor is sprayed with a lacquer or the like after the deposit of the developer powder thereon.

As previously mentioned the field electrode serves the function of providing a differential electrical field at or above its surface when it is part of the closed electrical circuit. Upon the application of an electrical potential to the field electrode, it is postulated that an effective space charge polarization exists adjacent the top surface of the field electrode in the relatively nonconductive areas (in the unexposed areas with photosensitive materials). The effective barrier at the surface enables negative carriers to accumulate and be trapped near the surface. In the conductive areas (light exposed areas with photosensitive materials), lowering of the barrier enables the mobile charge to pass through the electronic circuit rather than accumulate near the surface. It has been found that a number of materials will work as a photosensitive field electrode even though they do not show good photoconducting properties, for example titanium dioxide. With such photosensitive materials, illumination probably causes photodesorption of oxygen from the photosensitive particle. All of these materials have shown a change in volta potential (contact potential) with light. See Bell System Technical Journal, January 1953, vol. XXXII, p. 1 for definition and discussion. The volt potential is a measure of change of the surface potential or lowering of the effective surface barrier for charge flow. It is not necessary to produce more carriers throughout the field electrode layer with light as in the case with dye sensitized photoconductive zinc oxide, provided the number of available carriers in the nonexposed areas which are capable of being redistributed under an external field is sufficiently large or their drift mobility is high enough to cause rearrangement in the time required to cause field electrode polarization. Another manner of referring to the differential pattern on the field electrode is as a differential volt potential pattern. The light struck areas of the pattern have a volt potential change in the positive direction of at least 0.3 volt.

Thus, the photosensitive material in the field electrode should be of a semiconductive nature with the Fermi level sufficiently close to the conduction band so that the dark carrier concentration is sufficient to provide enough carriers for charge separation and surface trapping so that during development a space charge layer having a trapped concentration of sufficient magnitude is produced to cause a large field at the interface of the field electrode. During the subsequent step of transfer of developer powder from the field electrode to a transfer sheet, the mobility of the carriers should be sufficient to cause relaxation of the space charge layer so that charges are actually redistributed during the transfer step. However, the space charge layer is again reproduced on the next cycle when multiple copies are made. One point should be made clear, that is, that the field strength is only sufficient to cause the developer powder to adhere initially only when an external field is applied (dynamic system) and that the nature of the electrical phenomena involved is different than in the electrostatic process in which sufficient electrostatic charge always exists (static system) on the surface to pick up developer powder.

A field electrode capable of possessing a differentially conductive pattern may be constructed in various ways, for example, by the use of a photoconductive top layer on either an electronically conductive backing, such as paper, a metal plate, metallized paper or metallized plastic film, or on a relatively nonconductive backing such as Mylar film with or without a metallized back. The photoconductive layer may be integral with or separate from the backing. Such photoconductive materials may be vapor deposited upon the surface of either a flexible sheet or rigid plate, or such materials may be incorporated with an organic binder and applied to such a surface as a dispersion or slurry and dried. Examples of photoconductors suitable for the top surface of a photoconductive field electrode capable of producing a differentially conductive pattern upon irradiation, such as upon visible light exposure, include zinc oxide, cadmium sulphide, cadmium selenide, cadmium teluride, lead iodide and indium oxide, Such photoconductors result in a field electrode capable of having a change in transverse conductance on exposure to visible light. Nonphotoconductive semiconductors such as titanium dioxide and mercuric oxide result in a useful field electrode capable of having a change in surface conductance on exposure to visible light. Such nonphotoconductive semiconductive materials as titanium dioxide and mercuric oxide may also be used alone or in admixture with photoconductive materials. If the field electrode is to act as a master to make multiple copies, the photosensitive material should have a "memory" of at least 30 seconds or longer. In other words, the differentially conductive pattern in the photosensitive layer should persist for sufficient time to make the number of copies required. In use, such a photosensitive field electrode is dark adapted and then exposed to a visible light image in the absence of extraneous light to generate the differentially conductive pattern on the electrode.

Suitable organic binders useful to bond the photoconductor or semiconductor to the substrate or support of the field electrode should preferably be translucent or transparent and include such resins as the resinous copolymer of butadiene and styrene known as "Pliolite," silicone resin, polyvinylacetate, polystyrene, polyvinylchloride and polyvinylbutyral.

Certain organic materials, such as the oxalones and oxadiazoles, change their conductivity as the result of exposure to light and these also may be used alone or in combination with other ingredients on a suitable support for creating the differentially conductive pattern.

An example of a suitable photoconductive field electrode which has an appropriate resistance, memory, and ability to form thereon a differentially conductive pattern, e.g. by exposure to a visible light image or pattern, is an aluminized paper sheet or a polyester (Mylar) sheet upon which has been deposited a layer of zinc oxide admixed with an organic binder such as "Pliolite" (a copolymer of butadiene and styrene).

In another modification of the field electrode, the differentially conductive pattern is created on a metal plate by coating the metal plate with an insulating resin such as a silicone resin, polystyrene resin, a resinous copolymer of vinyltoluene and butadiene, and polymethacrylate, in a pattern to correspond to the graphic intelligence to be reproduced. This modification corresponds to a dry offset master.

The differentially conductive pattern may also be created by a heat pattern, such as exposing an alumina coated polyester film to an infrared pattern.

The required conductance of the substrate of, or the support for, the field electrode is usually accomplished by the type of material which makes up the electrode or support, such as metal, e.g. copper, iron, silver and aluminum. The substrate of the field electrode may be in the form of layers of conductive materials or as a single layer made from a single material or a mixture of materials. Since such conductive layer or conductive support is used to connect the electrical potential to the field

electrode, it should be at least as conductive as the conductive portions of the differential conductive pattern of the field electrode.

The field electrode may also include an integral backing for the conductive layer or as a supporting substrate. Such backings include wood pulp paper, rag content paper, various plastic films such as cellulose acetate and polyethylene terephthalate, cotton cloth, metal plate, metallic foil and glass.

The thickness of the field electrode sheet or the layers making up the field electrode depends to some extent upon the electrical characteristic 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 overall thickness of between about 1 and about 50 mils is preferred. The surface of the electrode should be extremely smooth to prevent entrapment of developer particles. Any pores or indentations in the surface of the field electrode should be smaller than the size of the developer particles.

The developer powder is preferably applied to the field electrode from a roller as an applicator, for example a roller made of or coated with conductive rubber or hardened conductive gelatin, a metal roller flocked with a 30 mil 1½ denier rayon filaments, or a magnetic roller covered with a thin layer of developer powder (at least 0.5 mil thick, preferably 20 to 30 mils thick). The developer applicator may also be an electrically conductive brush or a porous conductive roller with internally applied vacuum. Other types of applicators which may be used include an etched metal roller (rotogravure), or a conductive rubber or metal roller covered with a wire mesh or screen with means provided for adhering the developer to the roller surface. For high speed operations, satisfactory results have been obtained with a rotatable hollow nonmagnetizable metal cylinder containing within it a stationary permanent magnet having one pole thereof adjacent the inside cylinder wall at the point where contact is to be made with the field electrode. Magnetic developer powders must be used with a magnetic applicator. Speeds up to 55 inches per second of linear surface of the field electrode past the applicator have been achieved with a magnetic applicator, depending on the response time of the circuit.

The applicator or roller should be electronically conductive and offer the minimum resistance. The point to point electrical resistance of the roller from core or inner surface (the point of connection to the electrical potential) to outside surface should be between about 10^3 and about 10^5 ohms so as not to materially interfere with the voltage drop of the system but at the same time act as a current limiting element.

The roller or applicator must hold a thin layer of developer material on the surface thereof. The resistivity of the developer powder determines the type of applicator used. If the developer powder is highly resistant, then the developer powder layer on the roller should be thin. If the developer powder is highly conductive, then the developer powder layer on the roller may be relatively thick. The resistance of the circuit between the applicator and the field electrode should not be substantially greater than the conductive areas of the differentially conductive pattern of the field electrode. The cohesiveness of the developer powder will determine to some extent the thickness of the powder layer on the applicator. The conductive developer powder may be dispersed in a dielectric liquid such as a liquid silicone or heptane and applied to the developer roller without departing from the scope of this invention.

The use of the roller usually requires only slight pressure to allow the developer powder to contact the entire surface of the field electrode and the actual pressure used depends upon the amount of powder on the roller and the amount of surface to be covered. Actually, a minute gap at various places between the powder and field electrode will not necessarily prevent transfer of the developer powder. The roller can be supplied continuously with developer powder such as by the use of a well surrounding the lower portion of the roller and containing a mass of developer powder.

The electrical potential applied between the field electrode and the roller surface or transfer sheet is obtained from conventional sources such as batteries or rectifiers, etc. and should be of direct current, preferably a pulsating direct current 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 surface. Preferably about 100 to about 800 volts are utilized when the field electrode contains a metal layer directly below and in ohmic contact with the differentially conductive pattern. Preferably about 1500 to about 4000 volts are utilized when the field electrode contains an insulating layer, such as Mylar (resistivity of 10^{16} ohms for one square centimeter), between the conductive backing and the differentially conductive pattern. The amount of electrical potential necessary to achieve transfer of the developer powder to the surface of the electrode or transfer sheet depends upon various factors including the conductance or resistance of the surface to be coated, the chemical and physical nature (attractive forces) of the developer powder, the applicator and the electrode surface as well as the length of time of contact between developer powder and the surface to be coated (speed). Also the electrical potential will depend, to some extent, upon the difference in conductance between the conductive areas and nonconductive areas of the differentialy conductive pattern. The current passage from the surface of the differentially conductive pattern to the applicator during either development or transfer is as small as 5 to 10 microamperes (current density) and the observed current density is usually less than 100 microamperes.

After the differentially conductive pattern on the field electrode has been developed, the developer powder may be fixed to the field electrode to make the pattern permanent or it may be transferred to another sheet and then fixed. This transfer step from the field electrode to another sheet is an important aspect of the present invention and permits the production of multiple copies of the pattern using a single field electrode pattern. Normally this is carried out by passing the developed field electrode sheet face to face with a transfer sheet between two conductive rollers while applying an electrical potential of substantially the same magnitude as in the development step but of reverse polarity. In the case of utilizing photoconductive layer on the field electrode surface for producing the differentially conductive pattern by exposure to a light image or pattern, the application of a high electrical potential in the development step has a tendency to shorten the "memory" of the photoconductive layer thereby requiring reexposure. With many photoconductive layers which have been exposed to a light image, the differentially conductive pattern thus produced will persist for as much as 30 seconds or more permitting the production of many copies from the single exposure. This is particularly true of a photoconductive zinc oxide-resin binder layer. However, upon the application of a high electrical potential (300 volts or more) the differentially conductive pattern on the zinc oxide photoconductive layer is at least partially erased. Several techniques may be utilized to increase or retain the normal memory of such photoconductive layers after the development operation. The utilization of an insulating layer between the photoconductive layer and the backing or support of the field electrode minimizes the injection of charge carriers into the photoconductive layer from the backing as the result of the high potential of the field during the development step. A polyester film such as Mylar, for example, has been found to be a good insulating backing for a photoconductive layer. With the use of such an insulating layer between the field electrode support and the photoconductive layer, transfer can actually be effected in some instances by making a closed circuit contact between the conductive transfer rolls without the use of an external field. However, when a high potential field is utilized during transfer even the insulating layer of Mylar does not prevent faster decay than would be otherwise the case, and in most instances a reverse high potential electrical externally applied field is desirable and necessary for rapid transfer. To overcome and compensate for the effect of an applied electrical field, after development and before transfer, the imaged or developed field electrode is exposed uniformly to visible light, with the deposited developer powder acting as a light mask and only the previous light exposed areas receiving light. This maintains the differentially conductive pattern and overcomes the effect of the high potential during development and transfer in destroying or lessening the differentially conductive pattern.

When multiple copies are to be produced by transfer from the field electrode (master) many suitable and conventional sheet materials are available as the transfer sheet and in general the transfer sheet should be at least as resistive as the areas of the field electrode from which the powder is transferred. Wood pulp white paper, rag content white paper, polyvinylacetate film, and Mylar film are typical examples of good transfer sheets. The transfer sheets may be treated with a chemical to make the sheet slightly tacky or to cause a reaction with the developer to cause a visible and contrasting reproduction when the developer is not highly colored or is close to the color of the transfer sheet. The surface of the transfer sheet should be smooth as is the case of the field electrode.

Some papers or transfer sheets are not sufficiently resistive under high humidity conditions, thus poor transfer results. A method to by-pass this problem is by physically transferring these particles to a conductive intermediate roller and subsequently electrically transferring as above the image to plain paper. This procedure results in more complete transfer of the powder image. The roller that is used to physically remove the powder from the field electrode is a metal roller which is flocked with a 2 to 10 mil small diameter rayon fiber. The advantage of using this type of roller to a tacky conductive roller is that little or no image ghosting occurs.

When a positive is produced by making the insulating electrode sheet the cathode, the highest degree of polarization is observed on the relative resistive areas (unexposed) of the field electrode. The developer adheres in the most resistive areas and not in the conductive areas, whereby a visible positive pattern is produced corresponding to the differentially conductive pattern. As an example of a positive process, the field electrode is a photoconductive element comprising zinc oxide in an organic binder layer coated on aluminized paper. Good results are obtained using a dye sensitized French process zinc oxide dispersion coated on the aluminum layer of vapor coated aluminized paper. The coating weight of the photoconductive layer is about 3.5 grams/ft.^{2} on 45 pounds Crocker-Hamilton paper. The sensitivity of the paper increases with coating weight. Such a paper field electrode requires about 5 foot-candle seconds of incident light (tungsten) intensity to make the light exposed areas sufficiently conductive to prevent attraction of the developer powder when the electrical potential is applied.

The dark adapted photoconductive layer of the field electrode is exposed to a light pattern for a short duration (about one second) in the dark or under subdued light. Within the decay time of the light produced differentially transversely conductive pattern and while still in the dark, the field electrode in a horizontal position with the imaged side up is brought into contact with a conductive gelatin or metal roller covered with a thin layer of black cohesive developer particles having a conductivity of about 10^{-7} mhos per centimeter (by static test). A field of approximately +450 volts is applied to the conductive developing roller. The field is a 10 kc. pulsed signal. A black positive image results on the white photoconductive surface. A white receptor sheet of relatively high resistivity is brought into contact with the developed surface of the field electrode, and a reverse potential of −450 volts is applied by the use of a metal roller as the sheets are separated and most of the image is transferred to the receptor. If the developer powder contains a resin, it is then fused to permanentize the image. The photoconductive surface can be cleaned, dark adapted and reused. The differentially conductive pattern need not be confined to a photoconductive recording element. For example, a resin image on a metal support serves as a master for this system. Such plates can be used as an offset master for dry printing. The developer powder adheres to the resin or insulating areas and is subsequently transferred to ordinary paper. Thus, the field electrode used to modulate the selective adherence of powder materials may be created by a photoconductive material or by physical methods such as a resin image on a conductive backing.

In the case of preparing a negative reproduction by attaching the positive terminal of the electrical potential source to the aluminum layer of the photoconductive field electrode, the conductive areas are selectively coated because a high space charge is built up in the light struck areas when an N-type photoconductor is used to provide the differentially conductive pattern because such N-type photoconductors normally act as rectifiers under this condition. When the photoconductive insulating layer is the anode and an N-type photoconductor is used, the largest electrode polarization is obtained in the conductive areas (such as obtained by visible light exposure) increasing the attractive forces between developer powder and electrode surface, causing preferential deposition of developer powder in the light exposed areas. In general, the more conductive the powder, the more rapid the polarization, thus increasing the speed of the process.

For example, the negative process is accomplished when −450 volts from a pulsing D.C. source are applied to the developer applicator. The negative process does not work well unless a pulsing D.C. field is used. Polarization does not occur as rapidly for the negative process as it does for positive process, thus, development is at a slower rate, usually 2 to 3 seconds. The same light intensity and developer powder are used as in the positive process above.

FIG. 9 of the drawing diagrammatically illustrates, by an elevational side view partially in cross-section, suitable apparatus and process stages for the reproduction of a light image utilizing a photoconductive field electrode in accordance with the teachings of the present invention. According to FIG. 9 of the drawing, element **40** is a roll of photoconductive white sheet material **41** comprising a photoconductive zinc oxide Pliolite binder layer deposited (2.5 grams/sq. ft. dry) on a one mil Mylar film, the back of which has been vapor coated with a continuous aluminum layer, suitably supported within and attached to a hollow rigid drum or cylinder **42** having an insulated surface. Cylindrical drum **42** rotatable about its longitudinal axis has a flat section **43** and a suitable slot **44** for egress from and access to the interior of the drum whereby sheet **41** of photoconductive film is passed from roll **40** through the slot **44**, over suitable bearing roller **46** continuously onto flat section **43**, then over the exterior curved section of the drum **42**, and back through the slot **44** over a suitable bearing roller **48** to a storage roll **49** supported within and attached to the interior of drum or cylinder **42**. Elements **40**, **41**, **46**, **48** and **49** rotate with drum **42**. Element **51** is a conventional developed 35 mm. positive transparency containing an image thereon and element **52** is a conventional optical lens system suitable for projecting the image of film **51** by means of tungsten light source **53** onto the photoconductive layer of the field electrode sheet **41** on flat surface **43**. Element **54** is a soft electrically conductive rubber roller resting on the surface of photoconductive film **41** and grounded as shown. Section **56** of drum **42** is an electrically conductive metal backing making ohmic contact with the aluminum layer of photoconductive film **41** and is insulated from the remainder of drum **42** and capable of being grounded as shown upon rotating to the proper position. Element **57** is a hollow metal roller or cylinder having on its surface a layer of about 30 mils of magnetic black powder **58** having a conductive surface and a relatively resistive core and containing a stationary magnet (not shown) within it with one pole adjacent the contact point with drum **42**. The gap between the surface of developer roller **57** in the absence of developer powder and the surface of drum **42** is about 20 mils. Developer powder **58** is a 50–50 weight mixture of magnetite and Epon resin in fused spherical form (conductivity 10^{-8} mhos/cm.—static test) of 2 to 15 microns in size having on its surface and fused thereto a discontinuous layer of carbon black particles. Conductive developer roller **57** is connected to a positive unidirectional electrical potential source **59** of 4000 volts by means of a conventional electrical connection **61**. Section **56** is grounded as shown when it revolves opposite roller **57**. Element **62** is a tray for supplying additional developer powder **58** to developer roller **57**. Element **63** is a 40 watt tungsten light source and element **64** is a shield with a ⅛ inch slot therein width-wise across photoconductive film **41** to expose the photoconductive film **41** to light source **63**. Element **66** is a supply of transfer sheets **68** comprising 20 pound wood pulp bond paper, with suitable mechanism for supplying single sheets at a time at a rapid rate to the space between conductive roller **67** and photoconductive film **41** on the drum surface **42**. Conductive roller **67** is a gelatin roller covered with conductive 1.5 denier rayon flock 30 mils in depth. The transverse resistance of roller **67** is about 10 kilo-ohms. Section **56** (when it has revolved opposite roller **67**) is grounded while roller **67** is connected to a negative unidirectional potential of about 1500 volts as shown. Element **71** is the imaged transfer sheet which is then passed to a fixing station **69** for fixing the developer powder to the transfer sheet, such as by heating with an infrared lamp or with a hot air jet.

In operation, continuous reproduction is effected in the dark as follows: A section of dark adapted photoconductive film **41** is drawn from its interior roll **40** within drum **42** in a sufficient length to cover flat exposure section **43**. At this point the travel of the photoconductive film **41** is stopped and light **53** is turned onto project the image of transparency **51** through lens **52** to the surface of the photoconductive film at **43** to form a differentially conductive pattern on film **41** corresponding to the image of transparency **51**, the light struck areas becoming conductive. A light intensity of about 10 foot-candle seconds falling on the film plane has been found to be adequate exposure for film **41**. After this exposure, light **53** is turned off and the exposed section of the photoconductive film is drawn from exposure section **43** to the conductive backup plate of drum **42**. When the film is in position on this section **56** the entire drum is rotated, counterclockwise as shown, continuously at a rate of about 40 r.p.m. past developer roller **57** during the application of the electrical potential from source **59**. Roller **57** is rotating in a counterclockwise direction. Black developer particles **58** on the surface of roller **57** contact the entire surface of sheet **41** and deposit on the nonconductive (unexposed) areas of the differentially conductive pattern on film **41** produced as the result of the exposure at **43** to form a positive reproduction of transparency **51**. The gap between roller **57** and drum **42** is such that in relation to the depth of powder **58** on the surface of roller **57**, developer powder **58** is actually compressed. Any one point of film **41** remains in the field between roller **58** and drum **42** for no longer than about 5 milliseconds.

Drum **42** is continuously rotated past developer roller **57** and past light **63** which reexposes the conductive areas or previously light exposed areas having no developer powder thereon making such areas of optimum conductivity. On continually rotating drum **42**, section **56** with the positively developed photoconductive film **41** thereon passes to conductive transfer roller **67** while simultaneously a white sheet of transfer paper **68** is placed, face to face, with the developed photoconductive film containing deposited developer powder and as the drum continues to rotate without stopping is pressed between roller **67** which is at a potential substantially the same as the potential **59** but of reverse polarity. To achieve maximum resolution and no image explosion, transfer sheet **68** is brought into contact with the developed film **41** prior to the time the resulting sandwich is passed between roller **67** and drum **42**. As the drum **42** continues to rotate the image is transferred from photoconductive film **41** to transfer sheet **68** and the transfer sheet **68** is removed from contact with photoconductive film **41** while still in the electrical field of roller **67** and is then fixed in fixing station **69**.

Due to the persisting polarization of photoconductive film **41** and the charge retained by developer powder **58**, the developer powder **58** is attracted to and held to film **41** until the transfer step.

Drum **42** continues to rotate to its previous position for exposure and as it does section **56** contacts conductive rollers **54** which are grounded thereby bleeding off any charges which have been built up in the Mylar layer of photoconductive film **41**. In making multiple copies this grounding roller **54** improves the results by shorting out the surface and backing between the end of one cycle and before the start of another cycle. This type of operation is needed only with an insulating layer beneath the photoconductive layer. The purpose is to reduce the state of charge in the insulating layer so that film **41** will be presented to developer roller **57** at the same electrical condition on each cycle, otherwise fine lines of the latent image are lost and large image areas are "bleached" out.

Drum **42** is continuously rotated without stopping for reexposure and the cycle is repeated and the persisting latent image on photoconductive film **41** is again developed by developer roller **57** and the developed photoconductive film **41** is transferred to transfer sheet **68** by conductive roller **67** and the process is continued for as many copies as are needed.

The above described process of FIG. 9 of the drawings has the capability of producing about 80 to 100 copies per minute for over 5 minutes with such copies having a reflected optical density greater than 1.2, a resolution greater than 8 lines/mm. and a fog level less than 0.02 reflected optical density units above sheet color.

If a reproduction of a new image or pattern is desired, a new section of film **41** is again drawn upon surface **43** for exposure and repetition of the above sequence of steps. Excess film **41** on drum **42** is drawn onto takeup roller **49** for storage. Used film **41** which is stored on takeup roller **49** will in time become dark adapted and can be reused by reversing the rolls of film on rollers **40** and **49** when the supply on roller **40** has been exhausted.

The following examples are offered as a better understanding of the invention and are not to be construed as limiting the invention. The reproduction steps in the examples were 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 Pliolite in toluene, 30 parts by weight of acetone, and 4×10^{-4} grams of Phosphine R (C.I. 46055) per gram of zinc oxide as a 2% by weight alcoholic solution was ballmilled for 12 hours. The dispersion was coated 4 mils thick (wet) on an aluminum foil base and dried at room temperature with a subsequent dark adapting period of 12 hours. The process of dark adapting can be accelerated by heating the construction at an elevated temperature about 100° C. This white sheet (field electrode) was exposed to a projected positive image with 40 foot-candles falling on the photoconductive surface for one second. The transverse dark resistance for a one square centimeter surface area of photoconductive layer was 5×10^8 ohms and the resistance in the light exposed areas was 1×10^4 ohms for one square centimeter of surface area.

To develop the image on the field electrode, a potential of about +450 volts was applied to a conductive developing roller having a gelatin surface containing a layer of developer powder adhered thereto as the sheet was passed over the roller. The sheet was grounded during the operation. The developing roller was turning at a faster rate than the speed at which the field electrode sheet was moving and in the opposite direction while applying very light pressure to the sheet. The developer powder was black iron oxide covered with an Epon resin and had a particle size of about 25 microns and was prepared by spray drying a dispersion of the pigments in an organic solution of the Epon resin. The developer formulation is shown below:

(1)

	Percent
Epon 1004 (epichlorohydrin-phenolic)[1]	44
Magnetite (black iron oxide)[1]	52
Carbon black[1]	4

[1] Conductivity of 10^{-7} mhos/cm. (Static Test).

The powder image was then transferred from the field electrode to 20 pound white bond paper by applying a field of −1000 volts as the sheets pass through a set of metal pressure rollers, the roller making contact with the bond paper being connected to the negative terminal, and the field electrode carrying the powder image being grounded. When separated as they leave the rollers, the major portion of the black developer powder appeared on the white bond paper and was subsequently heated to fuse the resin and permanently affix the powder to the paper. The photoconducting element or field electrode may be cleaned and reused after dark adapting. The applicator roller can also be connected to the positive terminal and powder will transfer.

Other developer formulations and their conductivities (Static Test) which have been used in accordance with Example I are shown below:

(2)

	Percent
Epon 1004[1]	45
Magnetite[1]	30
Carbon black[1]	25

(3)

	Percent
Epon 1004[1]	50
Carbon black[1]	50

(4)

	Percent
Polystyrene[2]	65
Carbon black[2]	35

(5)

	Percent
Benzil[2]	65
Carbon black[2]	35

(6)

	Percent
Polystyrene[3]	50
Silver oxide[3]	50

Footnotes at end of example.

(7)

	Percent
Polyvinylbutyral[3]	50
Cuprous oxide[3]	50

(8)

	Percent
Polystyrene[1]	50
Copper[1]	50

(9)

	Percent
Magnetite[4]	50
Epon 1002[4]	50

(When used with a conductive flacked roller)

[1] Conductivity 10^{-2} mhos/cm.
[2] Conductivity 10^{-5} mhos/cm.
[3] Conductivity 10^{-10} mhos/cm.
[4] Conductivity 10^{-14} mhos/cm.

EXAMPLE II

In this example the same procedure was carried out as in Example I except that —500 volts of a pulsing D.C. field was applied to the conductive developing roller. Otherwise this system was processed the same as Example I, but resulted in a negative copy.

The above Examples I and II describe a process for placing an image on plain paper via a photoconductive field electrode. The photoconductive field electrode for this operation is reuseable. Thus, the photoconductive field electrode requires cleaning at the end of each cycle. This operation can be accomplished with a vacuum cleaner type apparatus. The photoconductive field electrode must be dark adapted or in other words the resistance of the light struck areas must be returned to their previous value before another cycle begins. With a zinc oxide photoconductive field electrode, this can be accomplished with time at ambient conditions or may be forcibly accomplished with heat. Thus, one may use a roll of photoconductive paper and allow the photoconductive decay to take place over a long time period. The other option is to use a drum or belt of material that would be forcibly dark adapted by heating at the end of each cycle.

The photoconductive field electrode as described in Examples I and II is especially useful in copying patterns with large black areas since the present process does not suffer from "halo" effects as occur in the electrostatic process. The transverse resistance of one square centimeter of area of this photoconductive field electrode should preferably be less than 1×10^7 ohms in the light struck area to prevent image deposition in the positive process and less than 1×10^7 ohms in the light struck area to cause image deposition in the negative process. This process shows a good gray scale with values of varying resistance below 1×10^7 ohms. The photoconductive material need not be limited to zinc oxide but to any photoconductive material which provides the above transverse resistance values for the field electrode and has sufficient decay time to allow development after exposure. Short decay materials may be used if exposure and development are simultaneous.

EXAMPLE III

An aluminum plate was imaged with a resin layer by a conventional photo-polymerization process. The resultant plate was similar to an offset plate. Copies were made from the plate as in Example I. The plate can be placed on a drum and repeatedly recycled to produce multiple copies by reapplying the powder developer and then transferring the powder image to paper and fusing.

EXAMPLE IV

A zinc oxide sheet prepared as in Example I was light exposed to a pattern under the same conditions as Example I and then developed by wiping a 5% aqueous solution of ethyl pyridinium bromide over the exposed surface of the sheet with a sponge connected to a +40 volts D.C. source and the sheet grounded. The resultant electrolytic deposited image was an insulator. The sheet was dried and heated to remove surface moisture. The developed sheet served as a dry offset master when processed according to Example III. The powder image corresponds to previously deposited insulating image of Example III.

EXAMPLE V

A dispersion of 33 parts by weight of photoconductive French process zinc oxide powder, 5 parts by weight of titanium dioxide, 16 parts by weight of 30% by weight of Pliolite in toluene, 3 parts by weight of polystyrene, 40 parts by weight toluene and 4×10^{-4} grams of Phosphine R (C.I. 46055) per grams of zinc oxide as a 2% by weight alcoholic solution was ballmilled for 12 hours. The dispersion was coated 3.3 grams/ft.^{2} (dry) on 45 pound Crocker-Hamilton paper which had been subbed with a 0.2 gram/ft.^{2} thick layer of cellulose acetate. The layer was dried and allowed to dark adapt for a period of 12 hours. The procedure of dark adapting can be accelerated by heating the construction at an elevated temperature of 70–100° C. This sheet was exposed to a projected positive image with 20 foot-candles falling on the photosensitive surface for one second.

The developer applicator is made of a metal roller on which the outer layer is a conductive plastic on which is flocked 30 mil rayon (1.5 denier) fiber. The roller is loaded with developer powder. The sheet is exposed to a projected image with 40 foot-candles falling on the photoconductive surface for one second. The sheet is passed between the developer roller and a metal backup roll at the rate of 5 inches per second. A potential of +1500 volts is applied to the conductive developer roller and the backup roller is grounded. The linear speed of the developer roller and the paper is equal.

The developer powder had an average particle size of about 10 microns. The developer formulation is shown below:

	Percent
Epon 1004 (epichlorohydrin phenolic)	44
Magnetite (black iron oxide)	52
Carbon black	4

This powder is made by spray drying this formulation from a solvent. The particles are spherical and have a pressed powder conductivity of about 10^{-9} mhos^{-1} cm.$^{-1}$. The powder is made cohesive by treating the powder in a fluidized bed with 0.01 cc. of castor oil per gram of powder. The cohesive powder results in a clean background print. The positively-imaged sheet is fused by passing it over a hot roller to fuse the image in place.

EXAMPLE VI

The same procedure was carried out as in Example V except that the developer roller is made of magnetic disks and covered with a thin aluminum foil. The powder is bladed to a thickness of 1/16 of an inch on to the developer roller. A potential of +2000 volts is applied to the developer roller. The powder used is the same as Example V except that the castor oil concentration is 0.004 cc./gram of developer powder.

EXAMPLE VII

A dispersion of 38 parts by weight of titanium dioxide powder, 16 parts by weight of 30% by weight Pliolite in toluene, 3 parts by weight of polystyrene, 40 parts by weight toluene and 4×10^{-4} grams of Phosphine R (C.I. 46055) per gram of oxide as a 2% by weight alcoholic solution was ballmilled for 12 hours. The dispersion was coated 3.0 grams/ft.^{2} (dry) on a 45 pound Crocker-Hamilton paper which had been subbed with a 0.2 gram/ft.^{2} layer of cellulose acetate. The layer was dried and allowed to dark adapt for a period of 12 hours. The dark transverse resistance of the sheet was 10^{-8} mhos per centimeter and did not change upon light exposure. This sheet is exposed to a projected positive image with 20 foot-candles falling on the photosensitive sheet for 8 seconds. The sheet was imaged as in Example V with good results. The surface resistance of the sheet in the light struck area was 2×10^9 ohms per square and in the unexposed area was 1×10^{10} ohms per square.

EXAMPLE VIII

This example was carried out the same as Example V, except that the developer powder was a finely divided metal salt. A color forming coreactant was an integral part of the field electrode sheet. The metal salt in this case was copper chloride and the coreactant was dithioxamide. The dithioxamide was 0.5% by weight of the solids in Example I. The imaged sheet was heated to 120° C. to develop a blue color in the unexposed area. This is an example of a complexing type color forming reaction. Oxidation-reduction type reactions will also work. For example, if a silver salt is deposited imagewise and a reducing agent is an integral part of the copysheet. Many other reactive combinations are possible, provided the powder has the proper conductivity and the coreactant does not harm the photoconducting properties of the photosensitive layer.

EXAMPLE IX

This example is the same as Example I except that a permanent nonphotoconducting pattern was made in the zinc oxide layer. Materials such as peroxides and primary amines destroy the photoconductive response of photoconductors. The use of such materials as the developer powder will produce the nonphotoconducting pattern, when developed in accordance with Example I. This resulting permanent pattern can be developed at a later time by uniform exposure of the entire sheet to light and then proceeding as in Example I after the exposure step.

EXAMPLE X

A 2 mil polyester film was dip coated with a 4% by weight dispersion of Baymal (colloidal alumina) and dried. The transparent sheet was passed through a commercial infrared copying machine in contact with an original. This transparency was then imaged with the magnetic roller and powder as described with regard to FIG. 9 of the drawings. The transparency was developed at the rate of 10 ins. per second at 2000 volts. The image was fused with heat. The heat pattern effectively decreases the surface conductivity of the hydrophillic Baymal layer.

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.

Various modifications and substitutions will become apparent to those skilled in the art without departing from the scope and teachings of this invention.

Having described my invention, I claim:

1. A process which comprises providing two adjacent surfaces, one of which surfaces contains an electronically conductive pattern and the other of said surfaces is uniformly conductive and contains thereon a uniform layer of conductive developer powder attracted thereto by a force greater than the force of attraction to said other surface, said electronically conductive pattern being defined by relatively conductive areas and relative non-conductive areas, said relatively conductive areas having a conductance at least about twice the conductance of said relatively non-conductive areas, providing an electronically conductive path between said surfaces, providing a uniformly distributed direct current electrical potential between said surfaces to create a differential electrical field whereby said conductive developer powder is differentially attracted to said conductive patterned surface to provide developed image areas corresponding to said conductive pattern, separating said surfaces while maintaining said electrical potential at the site of separation and discontinuing the electrical potential between said surfaces after separation whereby conductive developer material is held to the developed image areas of said conductive patterned surface by a force of attraction greater than the force of attraction exerted thereon by said uniformly conductive surface.

2. A process which comprises providing two adjacent surfaces, one of which surfaces contains an electronically conductive pattern and the other of said surfaces is uniformly electronically conductive and contains thereon a uniform layer of conductive developer powder attracted thereto by a force greater than the force of attraction to said other surface, said electronically conductive pattern being defined by relatively conductive areas and relatively non-conductive areas, said relatively conductive areas having a conductance at least about twice the conductance of said relatively non-conductive areas, providing an electronically conductive path between said surfaces, applying a uniformly distributed direct current electrical potential between said surfaces to create a differential electrical field whereby said developer material is differentially attracted to said conductively patterned surface to provide developed image areas corresponding to said conductive pattern, separating said surface while maintaining said electrical potential at the site separation, discontinuing the electrical potential between said surfaces after separation whereby developer powder is held to the developed imaged areas of said conductive patterned surface by a force of attraction greater than the force of attraction exerted thereon by said uniformly conductive surface, subsequently providing a third surface adjacent to the coated conductively patterned surface, applying a direct current electrical potential between said latter surfaces whereby the powder image is transferred to said third surface, and separating said latter surfaces while maintaining said electrical potential.

3. A reproduction process which comprises contacting a surface containing a differentially electronically conductive pattern and an insulating layer beneath the conductive pattern with an electronically conductive developer powder having a conductive surface and a relatively resistive core by rolling across such surface a roller applicator containing the developer powder on a uniformly electronically conductive surface of the roller held to said conductive roller surface by a force greater than the force of attraction to said conductive patterned surface to provide an electronically conductive path between said roller applicator and said surface containing said differentially electronically conductive pattern, said electronically conductive pattern being defined by relatively conductive areas and relatively non-conductive areas, said relatively conductive areas having a conductance at least about twice the conductance of said relatively non-conductive areas, applying a uniformly distributed direct current electrical potential between said surfaces during contact to create a differential electrical field whereby said developer powder is differentially attracted to said conductive patterned surface to provide developed image areas corresponding to said conductive pattern, separating said surfaces while maintaining said electrical potential at the site of separation and discontinuing the electrical potential between said conductive patterned surface and said applicator surface after separation whereby said developer powder is held to the developed image areas of said conductive patterned surface by a force of attraction greater than the force of attraction exerted thereon by said uniformly conductive surface.

4. A reproduction process which comprises exposing to a light image a first surface containing a photosensitive layer thereon and an insulating layer beneath the photosensitive layer to produce a differentially electronically conductive pattern in which the conductance of the light exposed area is at least twice that of the unexposed area,

contacting the light exposed surface with an electronically conductive cohesive developer powder having a conductive surface and a relatively resistive core by rolling across such surface a roller applicator containing the developer powder supported on a uniformly electronically conductive surface of the roller applicator held to said conductive roller surface by an applied force greater than the force of attraction to said conductive patterned surface to provide an electronically conductive path between said roller applicator and said photosensitive layer of said first surface, which uniformly conductive surface is at least as conductive as the light exposed area of said light exposed surface, applying a uniformly distributed direct current electrical potential of between about 10 and 5000 volts between said first surface and the uniformly conductive surface of the roller applicator containing the developer powder to create a differential electrical field whereby said developer powder is differentially attracted to said conductively patterned surface to provide developed image areas corresponding to said conductive pattern, separating said surfaces while maintaining said electrical potential at the site of separation and discontinuing the electrical potential between said surfaces after separation whereby conductive developer powder is held to the developed image areas of said conductive patterned surface by a force of attraction exerted thereon by said uniformly conductive surface, subsequently contacting the coated surface of said first surface containing the developer powder in the form of a pattern with the surface of a transfer sheet, applying a direct current electrical potential of between about 10 and about 5000 volts between said first surface and said transfer sheet during said contact whereby the powder image is transferred to said transfer sheet, separating said first surface from said transfer sheet while maintaining said electrical potential, and recovering said transfer sheet with the image reproduced thereon.

5. The process of claim **4** in which the surface containing the conductive pattern is a photoconductive surface.

6. A negative reproduction process characterized by making the conductive surface the cathode in the first transfer step and making the first receptor surface the anode in the second transfer step of the process of claim **4**.

7. A positive reproduction process characterized by making the conductive surface the anode in the first transfer step and making the first receptor surface the cathode in the second transfer step of the process of claim 4.

8. The process of claim **4** in which said developer powder is opaque to light and is deposited in the unexposed area of the photosensitive layer, and uniformly exposing to light the developed photosensitive layer containing developer powder.

9. The process of claim **4** in which the cycle of steps is repeated with the exception of the step of exposure of the surface to a light image whereby multiple copies of the original image are produced.

10. The process of claim **4** in which the developer powder includes a fusible resin and said imaged transfer sheet is fixed by heating.

11. A process which comprises providing two adjacent surfaces, one of said surfaces being uniformly electronically conductive and containing thereon a uniform layer of conductive developer powder attracted thereto by a force greater than the force of attraction to said other surface, providing an electronically conductive path between said surfaces, creating a differential electrical field between said surfaces during the existance of said conductive path and separating said surfaces while maintaining said differential field at the site of separation, such that developer powder is selectively attracted and transferred from the one surface to the other surface to provide developed image areas and is held to the developed image areas of said other surface by a force of attraction greater than the force of attraction exerted thereon by said uniformly electronically conductive surface.

12. The process of claim **11** in which said developer material is an electronically conductive developer powder containing a conductive surface and a relatively resistive core.

13. An electrographic reproduction process comprising:

(1) providing a first surface with an electronically conductive pattern, said pattern being defined by relatively conductive areas and relatively nonconductive areas, said relatively conductive areas having a conductance at least about twice the conductance of said relatively non-conductive areas,

(2) contacting said first surface bearing said electronically conductive pattern with an eletctronically conductive, rotatably moving applicator bearing a uniform coating of electronically conductive developer powder adhered to said applicator by a first attractive force to provide an electronically conductive path between said first surface and said applicator,

(3) concurrently with said contact imposing a uniformly distributed direct current electrical potential between said first surface and said applicator to create a differential electrical field whereby a second attractive force is created between said developer powder and said relatively non-conductive areas of said first surface, said second attractive force being sufficient in magnitude to overcome said first attractive force only in said relatively non-conductive areas, said first attractive force being greater than any force tending to cause said developed powder to transfer to said relatively conductive areas of said first surface, and

(4) separating said applicator from said photoconductive surface while maintaining said electrical potential at the site of separation whereby said second attractive force remains greater than said first attractive force such that said developer powder is retained on said relatively non-conductive areas of said photoconductive surface.

14. The process of claim **13** wherein said first attractive force opposes gravity.

15. The process of claim **13** wherein said first attractive forces opposes gravity and is magnetic.

16. An electrographic reproduction process comprising:

(1) providing a first surface with an electronically conductive pattern, said pattern being defined by relatively conductive areas and relatively non-conductive areas, said relatively conductive areas having a conductance at least about twice the conductance of said relatively non-conductive areas,

(2) contacting said first surface bearing said electronically conductive pattern with an electronically conductive, rotatably moving applicator bearing a uniform coating of electronically conductive developer powder adhering to said applicator by a first force opposite to forces favoring transfer of said developer powders to said first surface to provide an electronically conductive path between said first surface and said applicator,

(3) concurrently with said contact imposing a uniformly distributed direct current electrical potential between said first surface and said applicator to create a differential electrical field whereby a second force favoring transfer of said developer powder is created between said developer powder and said relatively non-conductive areas of said first surface, and a third force is created between said developer powder and said relatively conductive areas of said first surface, said second attractive force being sufficient to overcome said first force and said third force being insufficient to overcome said first force, and

(4) separating said applicator from said photoconductive surface while maintaining said electrical potential at the site of separation whereby said relative strengths of said first, second, and third forces are

retained such that said developer powder is retained on said relatively non-conductive areas of said photoconductive surface.

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CHARLES E. VAN HORN, Primary Examiner

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96—1; 117—17.5; 355—3.17; 118—637

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,563,734 Dated February 16, 1971

Inventor(s) B. 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 5, line 44, after "ductive" delete the phrase "patter have a maximum transverse resistance" and insert therefor -- area and powder is deposited only in the relatively --

Column 10, line 50, "volt" should read -- volta --.

Column 10, line 51, "volt" should read -- volta --.

Column 11, line 17, "teluride" should read -- telluride --.

Column 12, line 12, "characteristic" should read -- characte tics --.

Column 16, line 50, "onto" should read -- on to --.

Signed and sealed this 6th day of July 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER
Commissioner of Pat