# United States Patent [19]

**Kotz**

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[54] **ELECTROGRAPHIC DEVELOPMENT PROCESS**


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**Related U.S. Application Data**

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[52] **U.S. Cl.** ..... **96/1 R;** 96/1 SD; 117/17.5; 118/637

[51] **Int. Cl.** ..... **G03g 13/08;** G03g 13/22

[58] **Field of Search** ..... 96/1 R, 1 SD; 117/17.5; 118/637



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[57] **ABSTRACT**

An electrographic process involving the development of electrical potential patterns on a recording medium surface, for example electrostatic charge patterns on a photoconductive element, with electronically conductive, magnetically attractable toner material utilizing electrical forces generated by the electrical potential in the image areas of the recording medium to overcome a threshold magnetic counterforce exerted on the toner material by means of an electrical potential biased toner material applicator. The electrical potential pattern may be supplemented by a corresponding electronic conductivity pattern on the recording medium surface.


**19 Claims, 5 Drawing Figures**

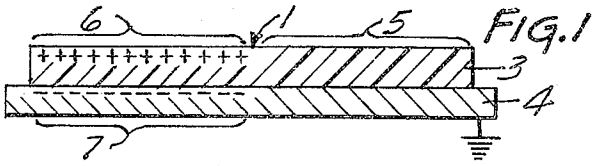



FIG. 1

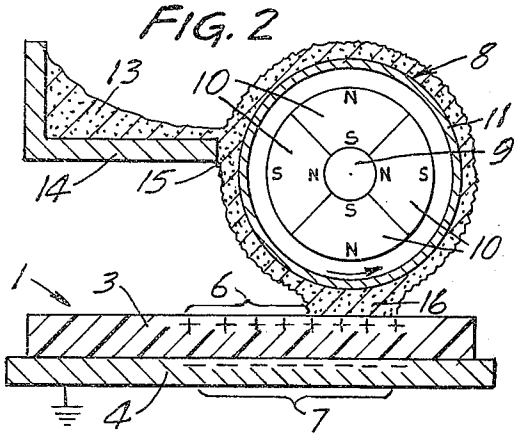



FIG. 2

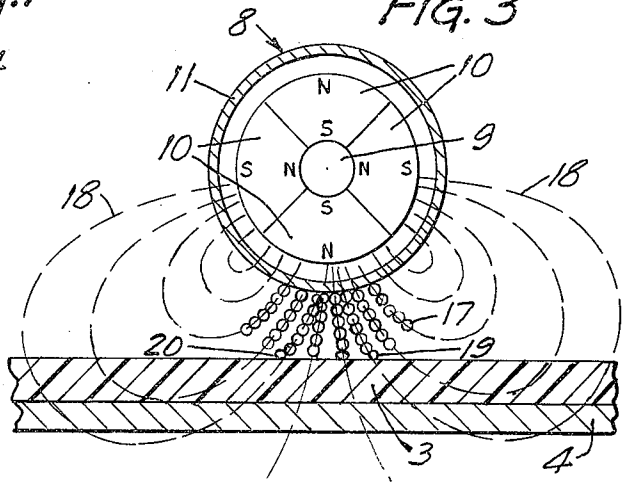



FIG. 3

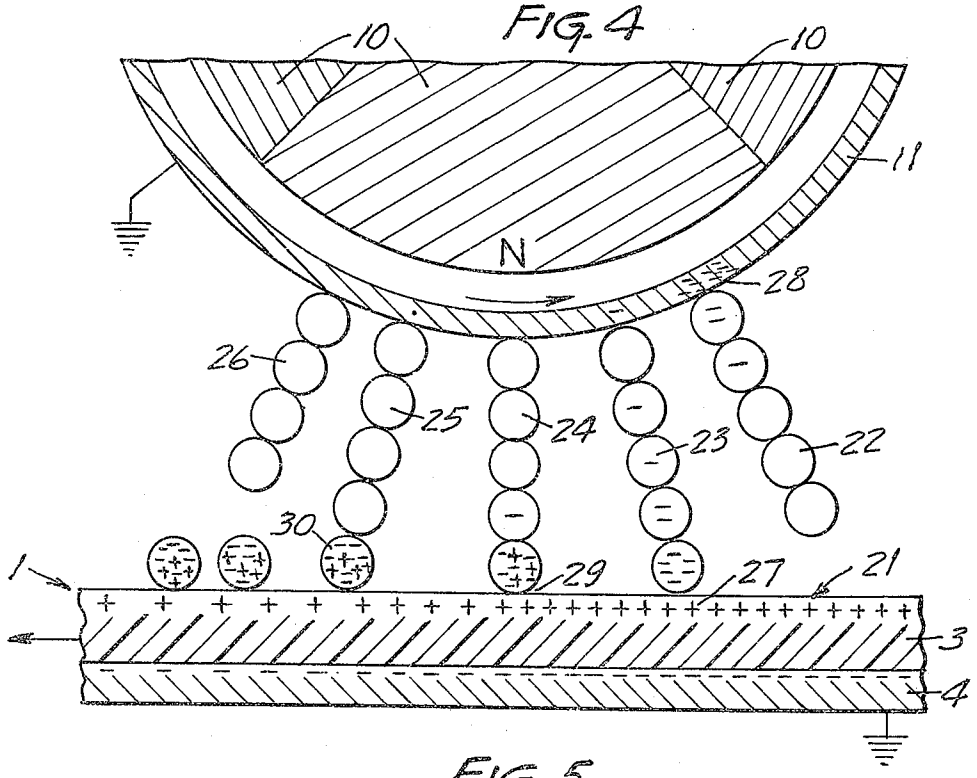



FIG. 4

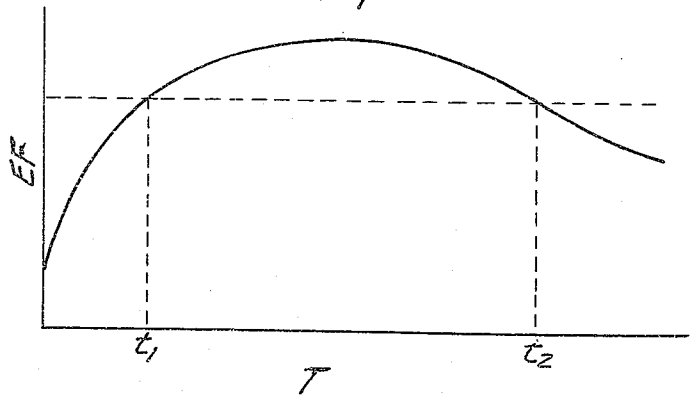



FIG. 5

# ELECTROGRAPHIC DEVELOPMENT PROCESS

This is a continuation of application Ser. No. 234,778 filed Mar. 15, 1972.

This invention relates to the electrographic development of latent images with toner or marking material, and particularly, to the development of latent images in the form of an electrical potential pattern under carefully controlled conditions to produce excellent quality likenesses of a desired configuration on a recording medium.

A vast majority of the electrographic copying processes in use today involve creation on a suitable recording medium of an electrostatic charge pattern corresponding to a pattern of light and shadow to be reproduced and the development of that pattern by deposition of marking material on the recording medium according to forces generated by such electrical potential pattern. Xerography is the most widely known of these techniques. The substrate may be photoconductive, such as in the case of selenium as taught in Carlson's U.S. Pat. No. 2,297,691, or may be a conventional insulating substrate overlying a photoconductive layer, as described in Watanabe, U.S. Pat. No. 3,536,483, to name a few examples.

After creation, the electrical potential pattern is generally developed by means of a finely divided developer powder thus giving form to the hitherto latent electrostatic image. In a common technique a fine, insulating, electroscopic powder is cascaded over the electrical potential pattern bearing member. The powder is, in the conventional use, triboelectrically charged to a definite polarity and deposits preferentially in regions of the surface where there is a preponderance of charge of the opposite polarity. The triboelectric charging is caused by presence of carrier beads in the powder mix. This technique of development is called cascade development.

In another form of cascade development, called magnetic brush development, magnetic carriers or magnetic toners are employed as in U.S. Pat. No. 2,846,333 to Wilson. In this technique a magnetic force is used to provide adherence of the toner-carrier mixture to a support member which is then presented to the image bearing member. While less efficient than conventional cascade development, magnetic brush development fills in solid areas better, is more compact, and does not depend on gravity to present the toner to the surface, a factor which allows freedom in locating the developer station.

In yet another form of electrostatic charge pattern development, a conductive one-component toner is used by bringing a conductive support member bearing a layer of fine conductive toner powder into contact with the charge pattern bearing member, as in U.S. Pat. No. 3,166,432 to Gundlach. In this case the toner is held to the support member by van der Waal's forces and the conductive support member is held at a bias potential during development. This technique fills in solid areas and requires only one component in the developer material.

A further method of developing an electrostatic charge pattern is to employ an electroscopic toner suspended in a liquid. With the proper choice of materials, the toner becomes charged to a definite polarity when dispersed in the liquid. When the electrostatic charge pattern bearing member is brought into contact with the liquid suspension, the toners deposit where there is a preponderance of charge of the opposite polarity as in cascade development.



While all of the above techniques have certain advantages in particular situations, each one suffers from disadvantages which impair their utility in actual machines.

In the conventional cascade development technique the toner-carrier combination has a definite charge polarity and is not reversible without changing the toner or the carrier. Thus, positive and negative developed images cannot easily be made. Also the images are hollow and solid areas are not filled in resulting in low-fidelity development compared to the original charge pattern. The triboelectric properties of the toner, while necessary to development, cause severe problems. Uneven charging of the toners causes backgrounding as do the uneven forces between carrier and toner result in varying threshold levels from toner to toner. Also, since the toner retains its charge for long periods of time, during cascading some toners escape the development region and enter other parts of the apparatus causing mechanical problems familiar to those skilled in the art. These problems, coupled with the inherent problems of using a two-component system where only one component is depleted, definitely limit the utility of such techniques.

The magnetic brush development, being a form of cascade development, suffers from some of the above mentioned disadvantages although it overcomes others. As mentioned above, this technique is less efficient but helps to fill in solid areas. However, it still requires triboelectric toners, usually with two-components, which have the concomitant problems mentioned above. Also, due to the mechanical brushing action and other electrical characteristics, this technique usually results in high background depositin and poor machine latitude.

The process described in Gundlach, U.S. Pat. No. 3,166,432, has many advantages over the above mentioned cascade type techniques. However, it suffers from severe drawbacks which limit its applicability. The van der Waal's forces, which act to adhere the toner onto the conductive support member, are a counterforce to the image producing electric force generated by the electrostatic charge pattern, and as such must be selectively overcome to have toner deposited. The van der Waal's forces are weak and non-uniform from one toner to the next. This small, poorly controlled counterforce gives high background deposition and poor machine latitude. See Orr, *Particulate Technology*, *MacMillan Co., N.Y.*, 1966, p. 406. Also high contrast is more difficult to achieve. The fact that the van der Waal's forces are not under direct control but subject largely to the surface properties of the materials involved makes the system highly susceptible to alteration of development properties upon wearing of the involved surfaces or variations in ambient conditions of temperature and humidity. It is also difficult to obtain a uniform, smooth layer on the conductive support member. All of these facts limit the utility of such a system.

In a liquid development technique most of the problems of cascade development are present in addition to other unique to a liquid system. The technique requires triboelectric charging, making image reversal difficult as explained above. Also, as in the case of cascade de-

velopment, the charge on a given toner is not well controlled, resulting in high background deposition, poor machine latitude, and a characteristic splotchiness in large dark or grey areas. The inherent problems of handling liquids, usually solvents, in a machine are also present.

In the present invention, two-component marking systems, the use of liquids, reliance or van der Waal's forces, and other detractive aspects of known electrographic techniques for developing electrostatic charge patterns are eliminated. It should be noted, moreover, that the present invention is applicable to the development of electrical potential patterns in general, regardless of whether provided by electrostatic charge as in conventional xerography or by some other equivalent means. The advantages accruing therefrom will be discussed in detail hereinafter.

In accordance with the present invention, a process is provided for applying toner material selectively to predetermined areas of a surface comprising:

1. providing a surface with areas thereof having an electrical potential in a range defining image areas and other areas thereof having an electrical potential in a range defining non-image areas, said areas defining an electrical potential pattern corresponding to the pattern to be produced,

2. contacting said surface with an electrically conductive support bearing a uniform quantity of magnetically attractable, electronically conductive toner material bound to said support by a magnetic force of attraction, such contacting providing an electronically conductive path between said surface and said support through said toner material, said support being at a direct current electrical potential of a magnitude and polarity such that the difference in electrical potential between said support and said surface results in a transient electrical transfer force on said toner material greater than and opposed to said magnetic force of attraction in said image areas and less than said magnetic force of attraction in said nonimage areas,

3. maintaining said electronically conductive path for a period sufficient to allow said transient electrical transfer force to be produced, and

4. discontinuing said electronically conductive path while said transient electrical force exists whereby said toner material is selectively deposited on said image areas of said surface.

As can be seen from the foregoing statement of the invention, a surface is provided with an electrical potential pattern which defines the areas which will utilimately receive the toner material (image areas) and those areas whic will not (the non-image or background areas). The technique for providing this electrical potential pattern may be any of the wide variety of known techniques.

For purposes of this invention, the surface upon which is formed the electrical potential pattern may be classified as one of two types, depending upon whether or not there exists in addition to the electrical potential pattern a coincident pattern of electrical conductivity corresponding in location to the electrical potential pattern. Certain surfaces do not provide a coincident electrical conductivity pattern; others do. Both types provide the excellent quality of recorded image characteristic of the present invention. As will be seen, however, certain distinctive advantages accrue from the type of surface employed.

An example of a surface which does not provide a coincident electrical conductivity pattern is photoconductive selenium such as is employed in many xerographic processes. The selenium is generally coated in 1 to 100 micron thicknesses on a conductive substrate, e.g., aluminum or other metal. The electrical potential pattern is typically provided by applying to the selenium surface a uniform electrostatic charge by a corona discharge device and then exposing the thus charged surface to a light pattern which results in charge loss in the light struck areas.

Another surface of this type is provided by a transparent electrically insulating film overlying a photoconductive layer, an example of which is a polyester film overlying a layer composed of photoconductive cadmium sulfide disposed in an insulating binder. Beneath the photoconductive layer is an electrically conductive substrate. Such constructions are described in U.S. Pat. Nos. 3,457,070 and 3,536,483. The transparent insulating film and the underlying photoconductive layer generally range in thickness from 10 to 60 micrometers. In these constructions, the electrical potential pattern is provided by applying a uniform electrostatic charge to the surface by a first corona discharge device, then simultaneously applying to the charged surface an electrostatic charge of the opposite polarity to the first charge, exposing the surface to a light pattern, and finally uniformly exposing the surface to light whereby the potential pattern is created. The electrically conductive substrate is at ground potential during both charging steps.

Still another example of this type, and not involving a photoconductive material, is an insulating layer such as a polyester film which is provided with an electrical potential pattern by selectively electrostatically charging certain areas of the surface by means of electrically conductive pins or styli. The dielectric layer typically covers an electrically conductive substrate. An electrical potential of at least about 250 volts relative to the conductive substrate is applied to the styli whereby electrostatic charges are placed on the dielectric surface in an imagewise pattern. Such electrostatic stylus recorders generally involve cascade electrostatic development of the charge pattern by triboelectrically charged toner powders as in U.S. Pat. No. 2,932,690, or liquid electrostatic development as in U.S. Pat. No. 3,540,412. Such electrostatic charge patterns on dielectric layers can easily be developed according to the present invention.

A further example of a suitable electrical potential pattern bearing surface is the imagewise electrostatically charged dielectric layer overlying a conductive substrate resulting from the imagewise ion projection of charged gas ions through an imagewise electrostatically charged screen according to the teachings of U.S. Pat. No. 3,582,206. Here, the original light image is projected onto an electrostatically charged photoconductive-coated screen. The final result, before development, is an imagewise charged dielectric layer (see Col. 5, lines 53–58) in one example, which would provide a suitable imagewise potential pattern for development by the teachings of the present invention.

Other surfaces of this type are provided by thin solid evaporated films including amorphous arsenic triselenide and amorphous arsenic trisulphide, and various coated organic photoconductors such as polyvinylcarbazole, poly-N-vinylcarbazole and others described in

U.S. Pat. Nos. 3,287,120 and 3,484,237, and British Pat. 990/368. Employing surfaces of the type not providing a coincident electrical conductivity pattern at the time the electronically conductive path through the powder is present in the operation of the process of this invention, the image and non-image areas of the surface have about the same electrical conductivity, which is preferably electrically insulating as defined herein.

An example of a surface which does provide an electronic conductivity pattern coincident with the electrical potential pattern is a layer comprising photoconductive zinc oxide disposed in an insulating binder, generally an insulating resin binder. This layer may overlie an electrically conductive substrate or there may be insulating layer between the photoconductive layer and the electrically conductive substrate. See U.S. Pat. No. 3,563,734 and U.S. application Ser. No. 820,062 now U.S. Pat. 3,764,313 for examples of such constructions. It should be noted that due to the sensitivity and controllability provided by the process of this invention, the photoconductive zinc oxide layer may be present in significantly reduced amounts relative to present constructions; less than 3 grams per square foot dry weight and generally less than 2.5 grams per square foot. This is advantageous from a cost and aesthetic standpoint, the latter because such a zinc oxide coated paper construction more closely approximates the feel of conventional bond paper. Other surfaces of this type are provided by a layer of photoconductive cadmium sulfide dispersed in an insulating resin binder and photoconductive titanium dioxide again dispersed in an insulating resin binder, each overlying an electrically conductive substrate.

A suitable technique for providing the electrical potential pattern employing surfaces of the type here under discussion is the application of a uniform electrostatic charge followed by exposure to a light pattern. At the time the electronically conductive path is present in the operation of the process of this invention, the surfaces of this type are defined by image areas which are relatively electrically insulating and non-image areas which are relatively electrically conductive as defined herein.

The photosensitive surfaces which do not provide a coincident conductivity pattern return to the dark, relatively insulating state in a brief time relative to the time between the exposure and development steps, the latter usually being about one second. Photosensitive surfaces exhibiting persistent electrical conductivity require times in excess of the time between exposure and development to return to the dark, insulating state.

As will be apparent hereinafter, various forces are at work in the operation of this process, all contributing to a carefully controlled set of conditions to provide maximum control over the application of toner material to the electrical potential bearing surface.

The following drawings are provided depicting the competing nature of these forces to the end that a sound understanding of the invention is provided. In these drawings:

FIG. 1 is a side elevational view of a recording medium bearing a potential pattern;

FIG. 2 is a schematic view showing development of the potential pattern on the recording medium of FIG. 1;

FIG. 3 depicts the influence of magnetic lines of force on the toner material during development;

FIG. 4 is a detailed illustration of the electrical forces present during development in accordance with the process of this invention; and

FIG. 5 is a graph of a plot of the electrical force on the toner material versus development time in the process of this invention.

Referring to FIG. 1, recording element 1 includes layer 3, which may but need not be a photoconductive layer as conventionally used in xerography, backed by a conductive layer 4 which is grounded. A potential pattern exists on the surface. In area 5 the charge has been dissipated whereas in area 6 the charge, along with the image charges 7, remains.

In FIG. 2, a development roller 8 is depicted including a long cylindrical magnetically permeable shaft 9 on which are mounted four long cylindrical sector-shaped magnet sections 10 coaxial to the shaft 9. The number of magnet sectors is chosen as four here only for purposes of convenience and illustration. The number may be more or less than this so long as toner transports smoothly around the shell 11. These sectors consist of a permanent magnetic material such as is commercially available under the tradename Plastiform. The magnets are magnetized uniformly along their length as indicated by the N,S designations in the diagram. Coaxial to, and surrounding, the magnet sections 10 is an electrically conductive hollow cylindrical shell 11 extending axially relative to said shaft and provided with a means not shown for connecting the shell to a unidirectional direct current electric potential or to ground.

A finely divided, magnetically attractable, relatively electronically conductive toner material 13, such as disclosed in U.S. Pat. No. 3,639,245 to Nelson, is placed in a reservoir support member 14, adjacent to but not touching the surface of shell 11. As shell 11 rotates (counterclockwise in FIG. 2) the toner material 13 is smoothly and uniformly dispensed onto the surface of the shell 11, being held in adherence thereto by the magnetic forces arising from the magnet sections 10. Developer roll may rotate in a clockwise direction if desired by dispensing the toner material 13 from a side opposite to that shown. The amount of toner 13 on the shell 11 can be controlled by the distance between the reservoir edge 15 and the surface of the shell 11. It has been found that, instead of rotating the shell 11, the shaft 9 and the magnet sections 10 attached thereto can be rotated while the shell 11 remains stationary. In the case illustrated, magnets 10 and shaft 9 rotate clockwise to transport the toner material 13 around the stationary shell 11 in a counterclockwise direction. Both techniques are applicable to this invention and work equally well in dispensing a smooth, uniform and well regulated supply of toner 13 from the reservoir 14. For the sake of definiteness we shall, in this embodiment, illustrate the former case wherein the shell 11 rotates while the shaft 9 remains stationary.

In operation, the development roller 8 is placed above the potential pattern bearing layer 3 of recording element 1 such that the axis of the development roller 8 is parallel to the plane of the potential pattern bearing layer 3 and placed at such a height above such layer that the uniform toner layer on the development roller 8 makes physical contact with layer 3 forming a well defined nip region 16. The development roller 8 is moved relative to the potential pattern bearing layer 3 in the direction shown while maintaining a uniform dis-

tance between shell **11** and layer **3** to provide a uniform electronically conductive path therebetween by means of the conductive toner material **13.** In this way, development of the potential pattern proceeds in time from one side of the recording element **1** to the other.

Due to the presence of the magnetic field the magnetic toner **13** in the nip region **16** forms into small chainlike groups **17** which follow the lines of magnetic force **18** between the shell **11** and the layer **3** as in FIG. **3.** These chainlike groups **17** become small electronic circuits between the shell **11** and layer **3.** The circuits are connected at the moment of physical contact of the toner **13** with layer **3** (**19** in FIG. **3**) and are disconnected when the contact is terminated (**20** in FIG. **3**). The formation of these chains has been observed by using a microscope focused on the nip region. Thus the magnetic sections **10** serve many purposes: to transport, uniformly and controllably, toner material around the conductive shell of the development roller, to create chain-like electronic circuits in the nip region, and to provide an uniform counterforce to the electrical development force.

To better understand the process by which development takes place reference is made to FIG. **4.** This description is idealized and simplified for the purposes of clarity, but illustrates the substantial phenomena about which this invention is concerned. Further details, extensions, and generalizations of this description will be apparent to those skilled in the art. FIG. **4** is a detailed illustration of the nip roller **16** during actual development. The recording element **1** is moving from right to left. The shell **11** is connected electrically to ground. The surface of layer **3** prior to development as at point **21** is uniformly charged to a surface potential $V_s$. The chain-like formations of toners **22, 23, 24, 25** and **26** represent progressive times or stages in the development process, **22** being the earliest and **26** being the latest. In actual practice there are many more toner chains set up in the nip region but they have been reduced, as have the number of toner particles in a chain, for purposes of illustration. The shell **11,** here shown as rotating counterclockwise, continuously presents fresh chains of toner material to the potential bearing surface. At chain **22** the above mentioned electronic circuit has not as yet been completed. However, due to the presence of the surface charge **27,** opposite polarity charge **28** is induced in the conductive shell **11.** This induced charge, chosen as negative here for purposes of illustration, immediately begins flowing through the chain towards the positive surface charge. This process takes place even after the toner chain contacts the charge bearing surface as in chain **23.** In chain **23** most of the negative charge has reached the end of the toner chain. At this stage, due to its opposite charges on the toner and the surface **3** there is an electrical force on the toner particle adjacent to the surface, such force being directed from the toner particle downward toward the charge bearing layer **3.** However, at a small time interval later, at the stage illustrated by chain **24,** another process begins to occur.

Since the toner is relatively conducting, some positive charge from the potential bearing surface **3** begin to leak onto the toner chain across the interface **29.** Equivalently, one can say negative charge leaks from the toner down onto the photoconductive surface. Either case leads to the same results but for the sake of this illustration the former is chosen. As this leakage occurs, the charge on the toner adjacent to the photoconductive surface begins to be neutralized and hence the electric force tending to pull the toner towards the said surface is diminished in time. Such charge leakage continues at a rate governed substantially by the electronic conductivity of the toner and the nature of the surface of layer **3.** The toner adjacent to the surface and the surface layer of the recording element itself form an interface region in which this charge transfer takes place. The rate of flow of charge (current) from surface to toner is determined by the effective capacitance and resistance of this interface. In general, the more conductive the interface region the faster will be the leakage across the interface.

At the next stage, illustrated by chain **25,** the toner chain is just ready to be pulled up by the magnetic counterforce, thereby breaking the aformentioned electronic circuit. At this stage there are two substantial forces acting on the toner **30;** one, the electric force due to the charge difference between the toner and the adjacent surface, the other, the uniform magnetic counterforce due to magnet sections **10.** The uniform magnetic counterforce acts as a threshold since all toners in which the electric force is greater than the magnetic counterforce will remain on the recording element surface and those in which the magnetic counterforce is greater than the electric force will be pulled up toward the magnet and not deposited on the recording element. The former condition is depicted here and toner material is thus deposited on layer **3.** The magnetic counterforce may vary spatially as one traverses the nip region due to the cylindrical or other geometry of the magnet structure, but the important point is that a definite and controllable counterforce exists everywhere in the nip and at the position of the separation point establishing a threshold counterforce to deposition at this separation point. Since the powder transport and nip region is well controlled, this is a constant and uniform threshold counterforce in time.

Since the electrical force on the toners adjacent to the recording element surface becomes greater as more charges of opposite polarities are present at the interface between the toner and surface of layer **3,** the more initial charge **27** on the surface of layer **3** that is present the larger will be the electrical forces on these toners. Hence, the more toners will remain on the surface of layer **3** after the developer roll assembly has passed by. Since a charge on the surface of layer **3** before development is usually related to a surface voltage it has been observed that as the initial surface voltage of the layer **3** increases, the amount of toner deposited also increases. When there is no initial surface voltage present or the surface voltage results in an electrical transfer force less than the magnetic counterforce, no toner material is deposited.

The time interval in which this process takes place, from the initial formation of the circuit until its termination, is about $10^{-3}$ seconds to about 1 second depending on the size of the nip region and the linear relative speed o the potential pattern bearing surface and the developer assembly.

In the above manner, high contrast, low background images are developed in which the solid areas are filled. The developed image may be fixed directly to the recording element or it may be transferred by conventional means to another substrate. Means for doing this are well known to those skilled in the art. The develop-

ment technique described in this embodiment is as efficient as the best previous techniques and allows for unusually high machine latitude.

The technique described in the above embodiment has been necessarily specific for purposes of illustration. Alterations, extensions and modifications of this technique would be obvious to those skilled in the art.

In this process, as can be ascertained from the above embodiment, the time in which the powder resides in the well-defined nip region in which an electronic circuit or path is formed is very important to the quality of development of the potential pattern. If the time is too short, the induced charges from the grounded conducting shell will not have time to reach the toners immediately adjacent to the recording element surface. If the time is too long, all of the charge on the toners will be neutralized by leakage of charge through the toner-recording element interface. This situation can be better understood by reference to the graph in FIG. 5. Here the electrical force (EF) on the toners adjacent to the potential bearing surface is plotted against the time since the formation of the chain-like circuit of which those toners are members. The uniform magnetic counterforce, which is approximately constant for this period of time, is superimposed but is directed opposite to the electronic force. For the toners to be deposited at the moment when the chain is pulled back to the developer roll, the electrical force must be greater than the magnetic force. Thus, in the instance graphed in FIG. 5, the nip time should be between $t_1$ and $t_2$.

The above embodiment can also be used to explain another advantage of this invention. By varying the electric potential of the conductive shell **11** in FIG. 4, variations in density in charged and uncharged areas may be accomplished. As the potential of the shell **11** (called a bias potential) is moved away from ground and towards the surface potential of the undeveloped surface of the recording element, the amount of toner deposited in those areas will diminish until, when the bias potential is at about the surface potential, no toner will deposit. However, in the undercharged areas, or those nearer ground potential, the higher the bias is raised the larger will be the potential difference between the developer roll and the recording element surface and, therefore, the more toner material will be deposited. This will lead to a reversed image.

In the following paragraphs we describe an embodiment of this invention employing a surface providing an electrical conductivity pattern coincident with an electrical potential pattern. FIG. 4 also applies to this case except that now, in addition to the surface of the recording element carrying a potential pattern, a conductivity pattern, conforming to the potential pattern, is also present. In this particular case, the non-image area is more electrically conductive, such as is provided by light exposure of a photoconductive surface, where there is little or no surface potential, and more insulating in the image areas where there is a high surface potential, such as is provided by non-light exposure of a photoconductive surface. It will be seen that the presence of this corresponding conductivity pattern, in addition to the potential pattern, acts to enhance the contrast and dramatically reduce background deposition.

In the case of a photoconductive surface, in dark areas the process is the same as in the first embodiment above. But in the light (and grey) areas another effect occurs which tends to reduce the amount of toner powder deposited there. Since, in these areas, the rate of charge leakage across the toner-surface interface is greater in these conducting areas, less electrical transfer force is built up. Thus, in these areas a higher surface potential is needed to develop the same amount of toner as in the first case. Or, likewise, for the same surface potential, less toner is deposited for the same nip time, toner electronic conductivity, and uniform magnetic counterforce. This conductivity pattern need not be present throughout the thickness of the photoconductor. All that is required is a surface conductivity pattern present at the time of development.

The same processes that occurred in the first embodiment also occur in this case but the leakage rate across the interface between the toner and the recording element surface is different. In a conductive area, the leakage and neutralization of the charge which is responsible for the electric force is much faster and thus for a given nip time (which is equivalent to a given development speed) less toner deposits than would deposit in the case where a conductivity pattern is absent.

In both of the above embodiments the conductive shell **11** and the conductive layer underlying the recording element surface layer have been electrically grounded through a connector. In the operation of this invention it is not necessary that such a ground connection be made as long as there is enough coupling to ground, either AC or DC, so that the currents described above will flow. The coupling may be accomplished, for example, by capacitive coupling or leakage conductance of the developer assembly support materials.

A suitable developer roll for supplying toner material to the electrical potential bearing surface is described in U.S. Pat. No. 3,455,276. Either the outer shell providing the support for the toner material or the enclosed magnetic force generating members may rotate. The magnetic counterforce is generally at least about $10^{-5}$ dynes in magnitude. This is to be contrasted with the far weaker van der Waal's forces relied upon in the process described in Gundlach, U.S. Pat. No. 3,166,432 (see especially Col. 7, lines 20–53).

According to Gundlach's teachings, one would expect that an applicator which applies a substantial counterforce to the deposition of toner particles on an electrostatic image would give inferior results. Surprisingly, according to the present invention a magnetic toner applicator used with magnetic, and simultaneously electronically conducting toner powder, gives improved quality copies with low background optical density due to unwanted toner deposition in background areas. Further benefits which result from utilizing this type of applicator are (1) the magnetic toner is easy to transport and contain without undue contamination of the machine interior due to weakly-bound or electrostatically charged toner particles floating about; (2) the development gap, that is the distance from the powder applicator electrode surface to the developable surface, can be quite large (many toner particle diameters) affording uncritical mechanical components. The magnetic applicator acting on the magnetically attractable toner causes the powder to stand up in chains and assures electrical contact from the applicator electrode to the developable surface. The gap should be between about $25 \times 10^{-4}$ cm and $50 \times 10^{-2}$ cm. In all cases, it should be at least equal to twice and preferably five times the dimension of the largest particles.

Further, this type of applicator and toner affords precise metering of a predetermined quantity of toner powder onto the applicator surface. For example, a doctor blade situated a fixed distance from the surface of a rotating cylindrical applicator, as in U.S. Pat. No. 3,455,276, meters out a constant supply of toner material onto the applicator surface. This assures a well-controlled contact nip between the powder and the developable surface as the two move relative to one another, and consequently assures a well-controlled development time, which is the time that a unit area of the developable surface is contacted by the above-mentioned nip of powder. The precise metering also assures a constant and well-controlled magnetic counterforce to be exerted on the powder particles.

In the practice of the present invention, the contact time, i.e. the duration of contact, between the toner-filled applicator electrode and the developer surface is very important. It must be long enough for the electrical transfer forces in image areas opposing the magnetic counterforce to build up sufficiently. It further must be short enough so they have not decayed below the threshold counterforce in these areas in the case where a decaying force is involved. This build up and decay of the electrical imaging forces is a function of the electrical conductivity of the toner material.

The magnetic applicator and associated toner metering devices, along with the well-controlled toner chains result in a well-controlled and reproducible conductivity of the toner powder in each incremental area of the nip region. The contact time, or duration, is also well controlled and reproducible. Typical nip widths (contact region) vary from about 0.1 cm to about 5 cm, and preferrably from about 0.2 cm to about 1 cm for cylindrical roll applicators. With the linear development speeds varying from about 0.5 cm/sec to about 200 cm/sec., and preferrably from about 1 cm/sec to about 100 cm/sec, these nip widths result in a contact duration time of from about $10^{-3}$ seconds to about 1 second and preferrably from about $10^{-2}$ second to about ½ second.

In Gundlach, U.S. Pat. No. 3,166,432, van der Waals forces are the preferred forces to hold the toner to the applicator electrode. These forces are quite weak, strongly dependent upon the distance between the toner powder and the applicator surface, and also strongly dependent upon the size of the toner particle. The van der Waals forces also vary considerably, being dependent upon the material and surface condition of the applicator surface as well as the toner. Furthermore, van der Waals forces do not lend themselves to uniform metering of controlled amounts of toner powder onto the applicator electrode surface. The weak forces and small particles (less than 20 microns and preferrably less than 5 microns, Column 7, lines 9 through 20) result in only a very thin layer of particles on the applicator surface. To contact the developable surface everywhere requires extremely well controlled mechanical tolerances to be maintained between the applicator electrode surface and the developable surface.

The substantial counterforce of the present invention results in a distinct threshold which must be overcome by imaging forces. There are at least two significant consequences of this not achieved by a process relying upon little or no counterforce. One is that background areas are cleaner, not having as many toner particles deposited due to mechanical forces, or even van der Waals forces between the toner particles and the developable surface, and the second is that the uniform counterforce assures uniform development of gray and black areas which would not be realized with no counterforce, or with a nonuniform or spurious counterforce.

A suitable magnetically attractable, electronically conductive toner material for use in the present invention is described in Nelson, U.S. Pat. No. 3,639,245. The toner material may have a static conductivity, as determined according to the technique described at column 3, line 54 – column 4, line 47 of U.S. Pat. No. 3,639,245, in the range of from $10^{-13}$ to $10^{-4}$ mhos/cm and preferably from $10^{-12}$ to $10^{-6}$ mhos/cm at an electric field of 100 volts/cm. Preferably, the conductivity of the toner material is electric field dependent and monotonically increasing with electric field in the range of 10 volts/cm. to $10^4$ volts/cm. Magnetic attractability is provided by inclusion in the toner material particle of a finely divided magnetically attractable material such as magnetite. The major dimension of the toner material particles may suitably range from about 0.5 micrometers to about 100 micrometers, preferably from about 2 to about 30 micrometers. Spherical shaped particles are preferred. Particles whose size is below 2 micrometers have been found to be subject to unpredictable and uncontrollable electrostatic and van der Waal's forces, resulting in higher background deposition and thus reduced quality. Particles above 30 micrometers limit resolution. Toner material which exhibits electric field dependency is highly conductive under developing field conditions when electrical current flow is desirable to create imaging forces and less conductive prior to and after development when the electric fields are substantially reduced and current flow is not desired.

The powder conductivity should be such that at high electric fields, as in image areas of the developable surface, it permits a relatively large current flow from the applicator electrode to the developable surface. However, the powder should not be so conductive that after one layer is deposited on said surface it thereafter electrically shields subsequent layers of powder from said surface, accepting their charge but preventing their deposition as would happen with a highly conductive powder. Additionally, at low or zero electric field, the conductivity should be considerably smaller so the powder which was deposited on the developable surface retains its charge for a time period sufficient to permit transfer of the powder from said surface to a receptor sheet.

Surfaces employed in the present invention which provide an electrical conductivity pattern have relatively conductive non-image areas and relatively insulating image areas as described in Shely, U.S. Pat. No. 3,563,734, incorporated herein by reference. The conductivity of the non-image areas, the light-struck areas when the surface is a photoconductive layer, ranges from about $10^{-17}$ mhos/cm. to about $10^{-7}$ mhos/cm. and the conductivity in the image areas, the non-light struck areas when the surface is a photoconductive layer, ranges from about $10^{-18}$ mhos/cm. to $10^{-9}$ mhos/cm., provided the non-image areas are at least twice, and preferably 100 times, as conductive as the image areas. The conductivity of the toner material should be at least 10, and preferably at least 100 times

as conductive as the image areas of the electrical potential bearing surface to be developed. It is further desirable, but not necessary, that the toner also be more conductive than the non-image areas.

The intensity of the light used to expose photosensitive surfaces in the practice of this invention will vary depending on many factors including the type of photosensitive element employed. A typical exposure range is from 0.05 to 20 foot-candle-seconds.

The electrical potential pattern to be developed includes areas which will provide a transient electrical force less than the magnet counterforce exerted by the toner material support (non-image areas) and areas which will provide a transient electrical force greater than such magnetic counterforce (image areas). The electrical potential difference between image and non-image areas depends upon the particular application and may be as small as **20** volts for some applications. A difference in potential of 200 volts is desirable in the case where the recording medium is a conventional photoconductor. Typically, the non-image area, in this case, is at a voltage of from a few volts to 50 volts and the image area is at a voltage of from 200 to 300 volts.

In the latter case the support bearing the toner material is biased to a potential within about 20 volts of the non-image area potential and at least about 20 volts different from the image areas at least in the case where the surface does not provide a coincident conductivity pattern. Preferably, in all cases, the applicator and the non-image areas are at substantially equal potential, and most preferably that is ground potential. The difference of potential between the applicator and a non-image area can be much larger in the case when the non-image area is conductive, i.e., when a conductivity pattern is present. The difference may be as much as several hundred volts since no powder will be deposited in a conductive region of the surface unless very much larger voltages are present. See Shely, U.S. Pat. No. 3,563,734. From a practical standpoint, this translates to greater processing latitude and sensitivity for the embodiment wherein a coincident conductivity pattern is present.

Most photoconductors are more sensitive while in the presence of an electric field and thus a photoconductor initially charged to 1000 volts would be more sensitive than the same photoconductor charged initially to only 500 volts. The same light exposure would give a difference of potential between light struck areas and dark areas of greater amount in the former case than in the latter. However, in the former case the final potential in the illuminated areas would not be about ground but at some potential other than ground even though the difference of potential between an unilluminated area and an illuminated area is greater for the same amount of light. The preferred potential for the non-image areas and the applicator is about ground potential and for the image areas about 200 volts or more. In some instances the non-image areas will not be at ground potential and in these cases the applicator is biased to a potential within about 20 volts of the non-image areas by a direct current power supply.

While overall, certain advantages are enjoyed by the embodiment of this invention wherein a coincident electronic conductivity pattern is provided corresponding to the ever present electrical potential pattern, there is an attractive feature distinctive to the other embodiment. That feature is the capability of producing either positive or negative images by varying the direct current electrical potential bias on the toner material support (developer roll). To illustrate, assume a potential pattern wherein certain areas of the potential bearing surface are at ground or zero potential and other areas are at a potential of +200 volts. In the case where the surface is a photoconductive surface, the areas at ground potential constitute light struck areas where an electrostatic charge has been dissipated and the areas at +200 volts constitute non-light struck areas. Of course, in a real situation, the surface potentials may vary over a wide range representing areas which have received varying amounts of light. Each potential will generate its own electrical transfer force, and depending on its magnitude relative to the magentic counterforce, such area will or will not receive transferred toner material. Positive images will be developed by biasing the toner material support to the potential of the light-struck areas, which in this hypothetical situation means holding the support at ground potential or within about 20 volts thereof in accordance with the above discussion. By the expedient of biasing the support to the non-light struck areas, however, the light struck areas of the potential pattern bearing surface may be developed, producing negative images.

Another method by which a potential pattern suitable for development by this invention involves uniformly precharging the outermost surface of a ferroelectric layer such as barium titanate by means of a corona discharge device. The layer is then selectively heated in an imagewise pattern to a temperature at which the dielectric constant increases substantially in the heated areas. This results in a potential pattern in which the differences in potential are caused by differing dielectric constant. The layer can then be developed by the means described in the above embodiments. Other techniques, based on similar concepts, are known to those skilled in the art.

The electrical potential bearing surface which is developed in accordance with this invention may constitute the ultimate record of the pattern to be produced or it may be an intermediate record wherein the developed image is transferred to another substrate. The imagewise deposited toner material may be fixed on a recording medium by any of the variety of conventional techniques. Toner material having a thermoplastic resin matrix is preferably fixed by conventional heat fusion, typical resins include B-stage phenol aldehyde polymers, polyvinyl acetate, and epoxy resins.

Examples of suitable insulating binders for the photoconductive materials employed in this invention include styrene-butadiene resins such as that sold under the tradename Pliolite S-7, polyethylene resin, chlorinated polyethylene, polyvinyl acetate, and Lexan (tradename) polycarbonate. In addition, a photoconductive layer may include various additives such as sensitizers, humidity control agents, and the like. The layer providing the electrical potential bearing surface may be applied to a variety of substrates including conductive paper, metals, paper-metal foil laminates, and metal coated resin films, or constructions of the above substrate including an insulating dielectric layer adjacent to the substrate.

The invention is further illustrated by the following examples wherein parts and percentages are by weight unless otherwise stated.

EXAMPLE 1

This is an example wherein a potential pattern not having a coincident conductivity pattern is developed. The photoconductor consists of a 15 micrometers thick layer of evaporated amorphous selenium having a conductivity of about $10^{-16}$ mhos per centimeter coated on a conductive aluminum backing. In the dark, the selenium surface is electrostatically charged to an electric potential of about +500 volts with respect to the conductive backing. The charging is accomplished by means of a corona discharge device drawn over the surface of the selenium layer. Thereafter the charged selenium surface is exposed to an imagewise pattern of light and dark; exposure in the light struck areas being about 0.5 foot-candle-seconds. The potential of the surface in the light struck areas is reduced to a potential of about +50 volts or less. Since, in the dark areas, the potential remains approximately the same, this exposure step results in the creation of a latent electrostatic image on the surface of the photoconductive selenium layer.

The potential pattern bearing surface is then moved past the developing station described and illustrated above. The distance between the surface of the conductive shell and the potential pattern bearing surface is about 0.07 centimeters and is uniform from end to end. The toner developing material is a thermoplastic, magnetically attractable, electronically conductive powder of the type described in U.S. Pat. No. 3,639,245. The static electrical conductivity of the toner material is about $10^{-11}$ mhos/centimeter at an electric field of 100 volt/cm. The size range of said toner material is from about 5 micrometers to 21 micrometers in diameter with an average size of about 13 micrometers. The magnets inside the conductive shell of the developer assembly are rotated at a speed of about 300 revolutions per minute and exert an average magnetic counterforce of about $10^{-4}$ dynes. The potential pattern bearing surface is moved past the developer assembly at a linear speed of about 15 cm./sec. The electrical potential of the conductive shell is held at about ground potential.

The resulting developed image pattern has toner selectively deposited on the above mentioned non-light struck areas whereas in the light struck areas where the potential is close to ground (+50 volts) no toner powder is deposited. Thus in this case the image areas are the high potential, non-light struck regions of the potential pattern bearing surface and the non-image areas are the low potential, light struck areas of the surface. The resulting image is of good quality, having high density in the image areas, low background in the non-image areas, and uniformly filled solid image areas. Also the continuous tone (grey scale) areas are well reproduced.

EXAMPLE 2

In this example, the bias potential of the conductive shell of the developing assembly is fixed such that negative images with respect to Example 1 are obtained. The procedure follows that of Example 1 except that during the actual development of the potential pattern bearing surface the electric potential of the conductive shell of the developer roll is fixed at a value about equal to the potential in the dark, non-light struck areas, i.e., about +500 volts. Thus the potential difference between the dark areas of the potential pattern bearing surface and the conductive shell is zero whereas in the light struck areas the difference is about −450 volts. The developing assembly is then moved across the selenium surface just as in Example 1. The resulting toner image pattern is a negative of the developed image pattern obtained in Example 1. Again the resulting toner image is of good quality with high density in the image areas and low background in the non-image areas, with solid areas being uniformly filled.

EXAMPLE 3

This example illustrates development of a potential patterned surface also providing an electronic conductivity pattern.

The photoconductor layer consists of zinc oxide dispersed in an organic resin binder and coated on a sheet of paper. The zinc oxide-resin layer consists of about 75% by weight of French process zinc oxide, about 15% by weight of an acrylic resin available under the tradename Arotap 3211, about 8.15% by weight of soy alkyd resin, and about 1.85% by weight of a mixture of sensitizing dyes consisting of about 30% by weight of Bromophenol Blue, 50% by weight of Sodium Fluorscein, and 20% by weight of Euchrysine GGNX. The photoconductive slurry is then coated out of a solution of toluene and methanol, onto 45 lb. paper bearing the trade designation CC base G rawstock (Weyerhauser). The layer of zinc oxide-resin has a dry weight of about 2.5 gm./sq. foot. The dark conductivity of the zinc oxide-resin layer is about $10^{-16}$ mhos/cm.

After dark adapting, the paper-zinc oxide-resin construction is electrostatically charged by a conventional corona device to an electric potential of about −500 volts relative to an electronically conductive backing plate contacting the underside of the paper substrate. The photoconductive surface of this photoconductive element is then exposed to an image pattern of light and dark; exposure in the light struck areas being about 10 foot-candle-seconds. This reduces the potential in the light struck areas to about −25 volts whereas the potential in the dark areas remains at about −500 volts.

The thus formed potential pattern is then developed by means of the developer assembly described and illustrated above. The potential bearing surface is moved past the developer assembly at a linear rate of about 3 inches/second; the distance between the surface of the developer assembly and the potential pattern bearing surface being about 0.085 cm. The toner developer material is the same as that employed in Examples 1 and 2. The developer assembly is held at an electric potential of about ground.

This process results in a developed image pattern on the pattern bearing surface in which toner is selectively deposited in the dark areas and no toner is deposited in the light struck areas. The toner is then fused onto the zinc oxide-resin surface by means of an infrared oven. The resulting copies have unusually low background in the light struck (non-image) areas and high density in the dark (image) areas. The solid image areas are faithfully filled, and the continuous tone areas (grey scale) are well reproduced.

EXAMPLE 4

A sheet of 0.0005 inch thick polyester film available under the tradename Mylar is coated on one surface with a thin film of electrically conductive aluminum

and wrapped around the periphery of a 4 inch diameter cylindrical aluminum drum with the aluminum coated side against the drum. The film composite is then taped in place. As the grounded drum rotates with a surface speed of about 5 inches/sec., a conductive copper wire stylus of about 0.01 inch diameter contacts the insulating polyester surface. A voltage of about +300 volts is applied to the wire stylus. A rotating shell, fixed magnet, magnetic developing station as described above contacts the polyester surface after the surface has been charged by the wire stylus. The cylindrical development electrode shell has its axis parallel to the aluminum drum axis and rotates at a surface speed of about 1.5 inches/sec. The magnetic developer powder is of the type described in U.S. Pat. No. 3,639,245 and has a static conductivity of about $10^{-6}$ mhos/cm. at 100 volts/cm. The powder applicator shell is grounded. Dense black lines are developed where the polyester was charged by the high voltage stylus, and virtually no powder is deposited elsewhere.

This invention is applicable to the development of potential patterns in general. We have illustrated this by electrostatic charge patterns but the concept is not limited to such patterns. Potential patterns may be created with uniformly charged (or uncharged) surfaces by varying the capacitance of the member upon which the potential pattern is to be produced. This can be seen by noting that $V = Q/C$ where V is the electrostatic potential, Q is the charge present on C, the capacitance of the member. We see from this relationship that V can be varied by varying either Q or C or both. Whereas most of the present applications of potential patterns involve varying the charge Q, varying the capacitance C is equally effective for producing potential patterns suitable for development.

What is claimed is:

**1.** A process for applying toner material selectively to predetermined areas of one surface of a layer of material comprising:

1. providing one surface of a layer of material with areas thereof having an electrical potential with respect to the other surface of said layer in a range defining image areas and other areas thereof having an electrical potential with respect to the other surface of said layer in a range defining non-image areas, said areas defining an electrical potential pattern corresponding to the pattern to be produced,
2. providing a cylindrical electrically conductive support electrically connected to said other surface with said support presenting a uniform quantity of one-component magnetically attractable, electronically conductive toner material bound to said support by a magnetic force of attraction which is uniform along the axial length of said cylindrical support,
3. arranging said electrically conductive support adjacent to and in spaced relation to said one surface at a uniform distance therefrom of at least twice the major dimension of the largest of said toner material whereby said toner material provides a electronically conductive path between said support and said one surface,
4. establishing said support at an electrical potential of a magnitude and polarity such that the difference in electrical potential between said support and said one surface, when the toner is presented in accordance with steps 2 and 3, induces a transient electrical transfer force on said toner material in said electronically conductive path, which for a period of time is greater than and opposed to said magnetic force of attraction in said image areas and less than said magnetic force of attraction in said non-image areas, and
5. progressively presenting said layer to said toner by providing unidirectional relative movement between said layer and said support with the axis of said support normal to the direction of the relative movement, said relative movement being at a rate such that said electronically conductive path
   a. is maintained for a period sufficient to allow said transient electrical transfer force which is greater than and opposed to said magnetic force of attraction in said image areas to be induced, and
   b. is discontinued while such level of said transient electrical force exists whereby said toner material is selectively deposited on said image areas of said surface.

**2.** The process of claim **1** wherein said image and non-image areas are electrically insulating while said electronically conductive path is present.

**3.** The process of claim **1** wherein at least said image areas are electrically insulating while said electronically conductive path is present.

**4.** The process of claim **1** wherein said image areas are electrically insulating and said non-image areas are electrically conductive while said electronically conductive path is present.

**5.** The process of claim **1** wherein there is a conductivity pattern corresponding to said electrical potential pattern while said electronically conductive path is present, said conductivity pattern being defined by relatively conductive areas in the non-image areas and relatively insulating areas in the image areas.

**6.** The process of claim **1** wherein said electrical potential pattern is provided by electrostatic charges.

**7.** The process of claim **1** wherein said one surface comprises photoconductive zinc oxide disposed in an insulating binder.

**8.** The process of claim **1** wherein said one surface comprises photoconductive selenium.

**9.** The process of claim **1** wherein said non-image areas are at an electrical potential of about ground.

**10.** The process of claim **1** wherein the difference in potential between image and non-image areas is at least **20** volts in magnitude.

**11.** The process of claim **1** wherein said one surface comprises a dielectric layer overlying a photoconductive layer..

**12.** The process of claim **1** wherein said electrical potential pattern is provided in accordance with an imagewise pattern of differing dielectric constant at said one surface.

**13.** The process of claim **1** wherein said magnetic force of attraction is at least $10^{-5}$ dynes.

**14.** The process of claim **1** wherein said non-image areas and said support are at about equal electrical potential.

**15.** The process of claim **1** wherein said non-image areas and said support are at about ground potential.

**16.** The process of claim **1** wherein said one surface comprises photoconductive zinc oxide disposed in an insulating binder and said non-image areas and said support are at about equal electrical potential.

17. The process of claim 1 further comprising fixing said toner material to said one surface.

18. The process of claim 1 further comprising imagewise transferring said toner material to a second surface.

19. The process of claim 1 further comprising imagewise transferring said toner material to a second surface and fixing said toner material on said second surface.

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