April 24, 1973 C. SNELLING 3,729,334

IMAGING PROCESS

Filed Dec. 30, 1970

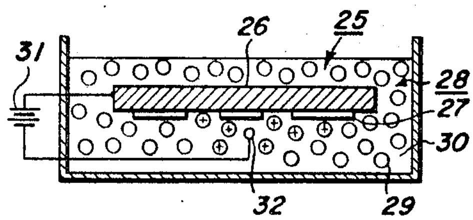

FIG. 1

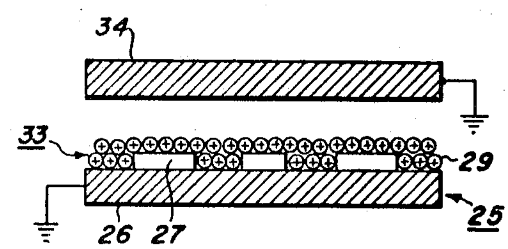

FIG. 2

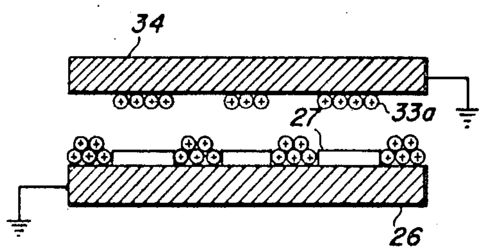

FIG. 3

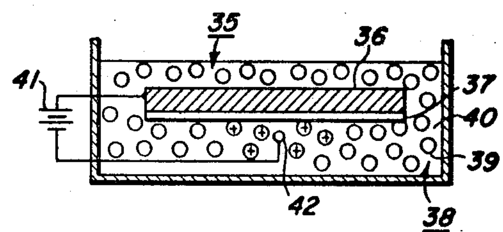

FIG. 4

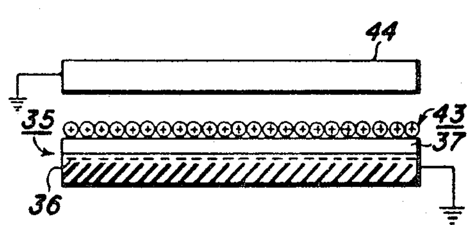

FIG. 5

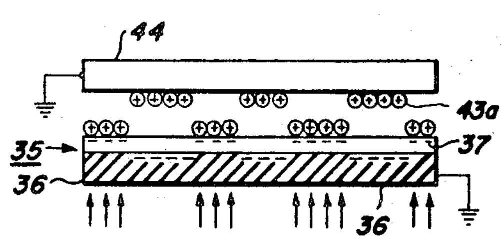

FIG. 6

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IMAGING PROCESS

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Continuation-in-part of abandoned application Ser. No. 707,575, Feb. 23, 1968. This application Dec. 30, 1970, Ser. No. 102,726

Int. Cl. B41m 5/00

U.S. Cl. 117—37 LE 1 Claim

ABSTRACT OF THE DISCLOSURE

The subject matter of the present invention is directed to a novel imaging system whereby a donor dispenser is utilized to deliver the developer particles of a liquid suspension in an imagewise manner to produce the final copy. An electrode configuration is provided, capable of establishing a non-uniform electric field within a liquid developer comprising uncharged developer particles. As a result of the established electric field within the system, the pigment particles present in the developer are uniformly coated on at least one surface of the dispensing master. The dispensing master is removed from the developer and delivers the developer particles in an imagewise manner to a suitable transfer sheet.

The application is a continuation-in-part of co-pending patent application Ser. No. 707,575 filed Feb. 23, 1968, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to an imaging system, and more specifically, to the application of non-uniform electric fields to electrostatic printing.

Many image and signal recording processes are known which involve the creation of electrostatic record from or by means of which a visible record may subsequently be formed. One such technique, a form of electrophotography, otherwise known as xerography, employs the use of a photoconductive insulating medium to form latent electrostatic images with the aid of electromagnetic radiation to produce a visible record. A second image forming process known as electrothermography relies upon a phenomena wherein certain dielectric layers, when charged electrostatically and heated, exhibit breaks in their respective charge temperature curves at a critical temperature, at which point the material experiences a sharp increase in conductivity. When exposed to heat in an imagewise configuration and the temperature exceeds the critical point for the particular plastic, the original charge is selectively dissipated in the heated, lower resistance areas. By dusting the remaining latent electrostatic image with a developer of the same charge, reversal development will occur in the now uncharged areas and a positive print obtained. A third imaging system useful for recording information termed chemography has been developed wherein irreversible chemical changes induced by light in specific materials can generate a persistent conductivity pattern which may be used for electrostatic imaging. Exposure to light in the absorption region for the particular material renders that material much more electrically conductive than before exposure. During or after exposure the film is sufficiently conducting so that, if an electrostatic charge is applied, it leaks off to ground in the exposed areas leaving an electrostatic latent image capable of visible development.

To visualize a charge pattern, and particularly when doing so in the art of xerography, it is usual to apply finely divided insulating materials, generally powders, to the charge pattern bearing surface. Thus, the electrostatic latent image is generally developed by cascading across

the image surface a mixture of relatively large carrier beads or granular material which carry on their surfaces finely diveded pigmented insulating developer particles. The developer or toner particles during development separate from the carrier beads and are drawn to the image charge on the image bearing substrate and thus there results, after cascading the mixture across the image bearing surface, a developed and visually apparent image conforming to the original image pattern. Alternatively, charge patterns have been developed using insulating or conductive toner or liquid ink by presenting the developer to the charge pattern bearing surface. As in the case of the cascading mixture, droplets or dust particles are drawn to electrostatic charge on the surface to be developed thereby resulting in a developed, generally visible image conforming to the original information. Other development techniques include the use of insulating developer particles on a brush, the use of magnetic particles in the form of a magnetic brush, and the application of a layer of insulating developer particles.

While these and other techniques have been found useful as image and single recording processes there are inherent disadvantages to their use. Generally there is the problem of unwanted particle deposition in the background areas. In addition, there has been encountered increasing difficulty in achieving tonal reproduction particularly in an area of half tone or continuous tone development. There has thus been devised a development system which employs relatively conductive particles on a relatively conductive base to avoid the cascading approach for developing an image. A developer dispenser is loaded generally by directing a powder cloud of the development material at the surface to be loaded or by cascading developer material across the surface of the respective dispenser. However, these particular techniques have specific disadvantages such as increased handling problems coupled with the difficulty of maintaining an efficient pigment concentration level. Liquid loading system have also been tried but these generally have been less successful since occasionally a developer dispenser loaded in such a manner will not readily release particulate material during development

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide an image forming system which will overcome the above noted disadvantages.

It is a further object of this invention to provide a novel method of providing an image reproduction.

Another object of this invention is to provide a novel method of developing an electrostatic latent image.

Still a further object of this invention is to provide a novel imaging system utilizing a liquid development process wherein the motion of electrically polarized matter in a non-uniform field serves as the development force.

The foregoing objects and others are accomplished in accordance with the present invention generally speaking, by providing a liquid developer comprising finely divided pigmented particles dispersed in a liquid generally having high electrical resistance. An electrode configuration is provided within the liquid developer such that a non-uniform electric field is established therein. A donor dispenser having on its surface a dielectric image is immersed in the liquid developer and electrically connected to at least one additional driving development electrode immersed in the liquid developer. The resulting configuration is such that a non-uniform electric field is established between the electrodes within the developer. As a result of the non-uniform electric field established, a charge is imposed on the pigment particles present in the suspension and the particles are directed toward the imaged dispenser-electrode. With the polarity such that the immersed development electrode is positive or negative and correspondingly the dispenser electrode negative or positive, the pigment particles plate out on the surface of the latter so as to load the dispenser to the desired level. The magnitude and polarity of the potentials utilized will vary depending upon the particular particle suspension system used. The loaded dispenser is then removed from the developer solution and subsequently utilized in a printing process. A conductive substrate is brought into contact with the loaded master and grounded, thereby transferring the pigment in a pattern conforming to the insulated or dielectric image of the donor substrate. Utilizing a conductive receptor in this manner, generally the resulting pigment particles will be next transferred to a final paper copy sheet. If it is desirable to eliminate the transfer step, then a conductive paper copy sheet itself may be used as the receptor.

In an alternative embodiment of the present invention the original developer dispenser may be replaced by a transparent photoreceptor. Selective transfer of the charged pigment particles according to an exposure pattern may then be realized.

A uniform electric field is one which exists between parallel metal plates that are oppositely charged. An uncharged or neutral particle will not move, but becomes polarized. Any other electrode configuration would necessarily produce a non-uniform electric field. Thus, the present invention excludes the utilization of an electrode configuration which yields a uniform field as stated above. The non-uniform field is produced as a result of the imbalance in the intensity of the field resulting from a difference in the concentration of the lines of force about the respective electrodes. The overall effect of the imbalance in the intensity of the field is to propel the developer particles through the carrier liquid to the surface of the electrode about which the field is weakest.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is further illustrated in the accompanying drawings in which:

FIGS. 1, 2 and 3 represent the process of the present invention as utilized in conjunction with a xero-print master, a dielectric image on a conductive support, as the donor dispenser substrate;

FIGS. 4, 5 and 6 represent the application of the process of the present invention in conjunction with a selective pigment release imaging process.

FIG. 1 represents the application of the process of the present invention wherein the developer dispenser member initially has formed on its surface in imagewise configuration a dielectric image. This dispensing member generally designated **25** comprises a conductive base support **26**, such as brass, with a dielectric image pattern **27** supported on its surface The dispenser member **25** is immersed in a liquid developer generally designated **28** comprising pigment particles **29** suspended in an insulating carrier liquid **30**. Immersed in the liquid developer **28** in a position beneath the dispensing member **25** and electrically connected thereto by voltage source **31** is an electrode unit represented as **32**. As a result of the non-uniform electric field established within the liquid developer between the immersed electrode **32** and the developer dispenser **25** the suspended pigment particles **29** rapidly coat the surface of the dispensing member **25**. Thus, for example, with the immersed electrode **32** maintained at a positive polarity and the dispensing member **25** at a negative polarity, positively charged pigment particles are uniformly deposited on the dispensing member thus providing a loaded developer dispenser.

Any suitable conductive substrate which will satisfy the requirements of the present invention may be used as the developer dispenser member. Typical conductive materials which may be utilized include: brass, aluminum, copper, steel, nickel, zinc and conductive glass. In addition, any suitable dielectric material may be used where applicable in the image development processes of the present invention. Typical dielectric materials include polyethylene, polyurethane, polyethylene terephthalate, polytetrafluoroethylene, cinnamate esters of polyvinyl alcohol and of cellulose, and Tedlar, a polyvinyl fluoride commercially available from Du Pont Corporation.

The coated dispenser **25** is removed from the liquid developer, partially dried and then, as represented in FIG. 2, the layer **33** of developer particles **29** brought into virtual contact with a general conductive substrate **34** with both members **26** and **34** being connected to ground. For purposes of this present illustration the conductive substrate **34** consists of an aluminized Myler (polyethylene terephthalate) material. However, other suitable materials may be utilized such as conductive paper and brass and aluminum foils as well as other related materials. Upon separation of the conductive member **34** from the developer dispenser **25**, as is represented in FIG. 3, the developer particles are transferred in an imagewise configuration **33*a*** to the surface of the member **34** conforming to the dielectric image **27**. Depending upon the type of substrate chosen as the receptive material **34** the image will be either fixed to the particular substrate or transferred to a subsequent support to which it will geenrally be fixed. With this in mind, a sheet like member may be interpositioned between the developer dispensing member **25** and the support **34**. Particles transfer to the interpositioned substrate in areas corresponding to the dielectric image. The sheet like member is characterized as sufficiently insulating to maintain a field therethrough. More specifically, the sheet like member should have a resisitivity upward of about 10^{10} ohms-cm. and pereferably in the area of about 10^{13} ohms-cm. and may comprise, for example, ordinary bond paper, and insulating plastic film such as cellulose acetate, polyethylene terephthalate, vinyl resins, cellophane and other cellulosic resins. The embodiment herein described is particularly useful in that it allows for the development of an image directly on the copy member which is to be used as the final print. Thus, the transfer step from the developed member during the printing phase of the process is avoided when this technique is utilized. In addition, cleaning steps which necessarily are required before a second image development process can be initiated are eliminated.

In FIG. 4 the developer dispenser **35** utilized comprises a substantially transparent conductive support substrate **36** with a thin photoconductive layer **37** overlying the respective surface, as indicated. The dispensing member **35** is immersed in a liquid developer **38** comprising developer pigment particles **39** dispersed in an insulating carrier liquid **40**. Immersed in the liquid developer **38** beneath the photoconductive layer of the dispensing member **35** and electrically connected thereto by voltage source **41** is an electrode unit **42**. As a result of a non-uniform electric field established within the developer solution particles **39** rapidly coat the photoconductive surface **37** of the dispensing member **35**. Thus, for example, with the immersed electrode **42** maintained at a positive polarity and the dispensing member **35** at a negative polarity, positively charged pigment particles are deposited on the photoconductive layer **37** of the support member. The loaded dispenser **35** is then removed from the liquid developer suspension and allowed to partially dry. As illustrated in FIG. 5 the photoconductive developer dispenser **35**, supporting the layer of developer pigment particles **43**, is brought into virtual contact with a transfer member **44**, such as a sheet or web of ordinary bond paper. While the print receiving sheet **44** is positioned against the developer layer **43** of the photoconductive dispenser member **35**, the photoconductive layer **37** is exposed to a pattern of electromagnetic radiation by projecting an image through the transparent support member **36** as demonstrated in FIG. 6. As a result of the exposure step and the resulting field differentials, the developer particles **43*a*** are transferred in the unexposed areas to the image receiving surface of substrate **44**.

The substrate **44** may preferably be at least partially conductive so as to present an equal potential surface to the charged developer particles. Any suitable material may be utilized such as aluminized Mylar, polyethylene terephthalate commercially available from E.I. du Pont de Nemours & Co., Inc., conductive paper, and other similar materials. With respect to the developing dispens-be used as a photoconductive layer **37** in conjunction tive material may be utilized as support substrate **36.** Typical materials include: Surlyn-A, a thermoplastic ethylene polymer commercially available from E. I. du Pont de Nemours & Co., Inc., coated with a conductive tetracyanoquino-dimethane complex commercially available from Eastman Kodak Co.; optically transparent glass coated with conventional conductive material such as tin oxide, copper, copper iodide, gold or similar materials; and metallized transparent films such as cellulose acetate (optical grade); polyesters such as Mylar, and polycarbonates such as Plestar commercially available from General Aniline and Film Co., overcoated by any suitable means such as by vacuum deposition with a metal coating such as aluminum, copper, gold, silver or chromium. In addition, any suitable transparent photoconductor may be used as a photoconductive layer **37** in conjunction with this structure. Typical photoconductor materials are doped polyvinyl carbazole, doped polycarbonates, selenium, selenium-tellurium alloys, selenium-arsenic alloys, cadmium sulfoselenide, phthalocyanine compositions and mixtures thereof. Typical doping agents which may be used when necessary are 2,4,7-dicyano trinitrofluorene, 2,4,7-trinitrofluoronone, tetrachlorophthalic anhydride, tetrachloro-p-benzoquinone and various mixtures thereof.

Following the particular development step of each of the specific processes described above the respective developed image, except where not necessary, is contacted with a secondary substrate or copy web and the developer pigment particles transferred thereto in an imagewise configuration by any suitable technique such as by electrostatic transfer, pressure transfer or adhesive pickoff. Typical materials that may be used as a transfer substrate include: polyethylene terephthalate, polyvinyl fluoride, polyurethane, polyethylene, and ordinary bond paper. Any suitable means may be used to fix the resulting image formed on the transfer material such as by placing a lamination over the top surface of the image particles or by heat or vapor fusing of the resulting image to the particular transfer substrate.

It is to be noted that although the dispenser member of the present invention is illustrated in the form of a flat plate it may take many other shapes including that of a rigid cylinder or a flexible endless belt-like configuration.

The liquid developer of the present invention comprises a suspension of finely divided particles in a dielectric liquid. Any suitable organic liquid having a high volume resistivity, preferably at least about 10^9 ohms-cm. or greater and a low dielectric constant preferably less than about 3.4, may be used in the course of the present invention. Typical liquids include aromatic hydrocarbons such as benzene, toluene, and xylene; aliphatic hydrocarbons such as hexane, cyclohexane, and heptane; halogenated hydrocarbons such as trichloroethylene or carbon tetrachloride; silicon oils and mixtures thereof. Other saturated hydrocarbons include decane, dodecane, n-tetradecane, molten paraffin, molten beeswax, and other molten thermoplastic materials, Sohio Odorless Solvent, a kerosene fraction commercially available from Standard Oil Co. of Ohio, Isopar G, a long chain saturated aliphatic hydrocarbon commercially available from the Humble Oil Co. of New Jersey, and mixtures thereof. Other substantially insulating carrier liquids comprise generally non-volatile, unsaturated natural occurring oil-like organic compositions having a hydrocarbon nucleus. Typical materials include olive oil, castor oil, linseed oil, peanut oil, corn oil and soybean oil. These compositions generally fall into the class of compounds known as glyceride esters of unsaturated fatty acids and with one or more of the hydroxyl groups of the glycerol constituent have been replaced by an acid radical. Other naturally occurring compounds which have been found useful include cotton seed oil and china wood oil derived from the seeds of plants; pine oil and cedar wood oil which are generally terpene compounds; and marine oils such as sperm oil and cod liver oil.

Any suitable pigment or pigmented particle which may be suspended in the insulating liquid may be utilized. Typical particles are talcum powder, charcoal, aluminum, bronze, sulfur, pulverized resins of all varieties such as ordinary rosin, sealing wax, coumarone indene resin, treated pine resins sold under the trademark Vinsol resin and various other synthetic and natural resins. Hard waxes have also been found suitable. Powdered dye may also be used or the resin or other powder used may be dyed any color desired. For example, the Vinsol resin may be melted with a small proportion of Nigrosine dye, cooled and pulverized to give a dark colored powder. Other pigment materials that may be utilized include: titanium dioxide, zinc oxide, zinc sulfide, iron oxide, chromium oxide, lead chromate, zinc chromate, cadmium yellow, cadmium red, red lead, antimony dioxide, magnesium silicate, calcium carbonate, calcium silicate, phthalocyanines, benzidenes, denitranilines, naphthols, toluidines, carbon black, and Monterey Red pigment. When used under proper conditions, such as in the absence of illumination, then other photoconductive pigments may also be used in conjunction with the present invention. Typical such pigments include quinacridones such as 2,9-dimethyl quinacridone and 4,11-dimethyl quinacridone; anthraquinones such as 1,5-bis(beta-phenylethylamino)-anthraquinone; 4-(2′-hydroxy-phenyl methoxy amino)-anthraquinone; azo compounds such as 2,4,6 - tris(N-ethyl-N-hydroxy-ethyl-p-aminophenylazo)-phloroglucinol, and 1,3,5,7 - tetrahydroxy - 2,4,6,8-tetra-(N - methyl - N - hydroxyethyl-p-aminophenylazo)-naphthalene; phthalocyanines such as beta form metal free phthalocyanine, copper phthalocyanine, and the x-form of metal free phthalocyanine as described in copending application Serial No. 505,723 filed October 29, 1965 now U.S. Patent No. 3,357,989; polyvinyl carbazole and suitable charge transfer complexes such as phenolaldehyde resins, phenoxies, epoxies, polycarbonates, urethanes, styrene or the like complexed with electron acceptors such as 2,4,7-trinitro n-fluoronone and 2,4,5,7-tetranitro-9-fluoronone.

A wide range of voltages may be employed in the present system. The applied potential necessary in order to coat the developer dispenser will vary depending upon the spacing of the dispenser with respect to the immersed developing coronode and the length of time that the dispenser support is left to be exposed to the liquid developer system. Generally speaking, the active surfaces of the immersed electrodes will be positioned about 5 to about 50 mm. apart with preferred operational conditions being from about 10 to about 20 mm. Operating within this framework at voltages of from about 4 kv. to about 10 kv. generally the developer dispenser will be left exposed in the liquid developer for about .5 to about 5 seconds. Under the above mentioned preferred distances the voltages utilized will be about 7 kv. for about 2 seconds.

Although the immersed development electrode of the present invention is illustrated as a single electrode any suitable configuration and number of electrodes may be employed to provide the desired non-uniform electric field. Thus, a series of needle-like electrodes or knife edge electrodes may be employed to provide the necessary field and current density, a thin wire electrode may be used such as a corotron wire or a number of wire electrodes.

As discussed above, the structural relationship of the driving electrode with respect to the imaging electrode will be such so as to establish a non-uniform electric field within the developer as a result of the imbalance in the concentration of lines of force per unit area of electrode. The configurations will be such that the intensity of the field will be highest in the vicinity of the driving electrode and diminish in strength as the imaging electrode is approached. This will produce the imaging effect desired.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

To further define the specifics of the present invention the following examples are intended to illustrate and not limit the subject matter of the present invention. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

A 1% solution of Monterey Red X2277 pigment in Isopar G is prepared. A brass substrate having a dielectric image consisting of a KPR dielectric pattern on its surface is immersed in the liquid developer solution. A needle electrode is immersed in the liquid developer about 1 cm. beneath the substrate and a voltage of about 10 kv. applied to the immersed coronode for about 10 seconds. The entire surface of the brass-KPR imaged substrate is coated with Monterey Red pigment particles. Following deposition of the pigment particles on the imaged surface the brass substrate is removed from the liquid developer and allowed to partially dry for about 5 seconds. An aluminized Mylar sheet is placed in contact with the loaded master and connected to ground. Upon separation toner particles are transferred to the surface of the Mylar sheet in an imagewise configuration conforming to the original dielectric pattern on the brass donor dispenser. The images were vapor fused to the Mylar substrate.

EXAMPLE II

The process of Example I is repeated with the exception that the image is tape transferred from the Mylar substrate. Images of high density and resolution were obtained.

EXAMPLE III

A NESA glass electrode coated with a thin layer of polyvinyl carbazole doped with trinitrofluoronone is immersed in a 1% solution of Monterey Red pigment in Isopar G. A needle electrode is immersed in the liquid developer beneath and facing the photoconductive surface of the NESA glass electrode. The needle is spaced approximately 1 cm. from the photoconductive surface. A potential difference of about 10 kv. is applied for about 10 seconds across the interface with the polarity of the needle being positive and that on the NESA electrode a negative. A layer of Monterey Red pigment particles is deposited on the photoconductive surface of the NESA electrode. The NESA electrode is then removed from the liquid developer and allowed to partially dry for about 5 seconds. The loaded donor dispenser is then connected to ground and an aluminized Mylar sheet placed across the surface of the pigment particles. The transparent surface of the NESA glass is exposed to an electromagnetic radiation source in the manner of contact exposure which causes selective migration of charge from the interface between the NESA surface and the photoconductive surface to the interface between the photoconductive surface and the pigment particles. The aluminized Mylar substrate is then removed from the surface of the donor dispenser with pigment particles in the unexposed areas adhering to the Mylar substrate. Images of high resolution and density are obtained.

Although the present examples were specific in terms of conditions and materials used, any of the above mentioned materials may be substituted when applicable with similar results being obtained. In addition to the steps used in the process of the present invention, other steps or modifications may be used, if desirable. By reversing polarities in the system, reversal development imaging may be realized. In addition, other materials may be incorporated in the liquid developer imaging members, donor supports, pigments, and colorants which will enhance, synergize, and otherwise desirably affect the properties of the present invention. For example, the consistency of the liquid developer may be controlled by the addition thereto of various amounts of thickening agents.

Anyone skilled in the art will have other modifications occur to him based on the teaching of the present invention. These modifications are intended to be encompassed within the scope of this invention.

What is claimed is:

1. A method of image development comprising:
   - (a) immersing a conductive dispensing member in a liquid developer suspension comprising developer particles dispersed in a dielectric carrier liquid, said dispensing member comprising a conductive substrate with an insulative image on the surface thereof, and said developer suspension having pre-disposed therein at least one electrode electrically connected to said dispensing member, said dispensing electrode and said immersed electrode jointly capable of establishing within said suspension a non-uniform electric field as a result of an imbalance in field intensity about said dispensing member and said immersed electrode;
   - (b) applying an electrical potential to said dispensing member and to said immersed electrode so as to establish a non-uniform field within the developer suspension and thereby causing uniform disposition of charged developer particles on the image bearing surface of said dispensing member;
   - (c) positioning the image bearing surface of the dispensing member laden with charged developer particles in juxtaposition with a substantially conductive substrate;
   - (d) grounding said dispensing member and said conductive substrate; and
   - (e) separating said dispensing member and said conductive substrate to produce an image corresponding to said insulative image.

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CHARLES E. VAN HORN, Primary Examiner

U.S. Cl. X.R.

96—1R, 1.4; 117—93.4; 204—181

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,729,334 Dated April 24, 1973

Inventor(s) Christopher Snelling

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

Column 2, line 3, kindly delete the term "diveded" and substitute therefor --divided--.

Column 3, line 17, kindly delete the term "alternative" and substitute therefor --alternate--.

Column 4, line 12, kindly delete the term "Myler" and substitute therefor --Mylar--.

Column 4, line 24, kindly delete the term "geenrally" and substitute therefor --generally--.

Column 5, line 8, following the term dispens-, kindly delete the phrase"be used as a photoconductive layer 37 in conjunction" and substitute therefor --sing member 35 any suitable optically transparent conduc- --.

Signed and sealed this 17th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents