# United States Patent [19]

**Rutherford et al.**

[11] **3,830,648**

[45] **Aug. 20, 1974**


[54] **PHOTOCONDUCTOR-GLASS BINDER PLATE WITH INSULATING RESIN IN PORES**


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[73] Assignee: **Varian Associates,** Palo Alto, Calif.



[22] Filed: **Jan. 12, 1973**

[21] Appl. No.: **322,996**

**Related U.S. Application Data**

[63] Continuation of Ser. No. 131,385, April 5, 1971, abandoned.

[52] **U.S. Cl.** ..... **96/1.5,** 96/1.8, 117/98 R, 117/124 E, 252/501, 117/34

[51] **Int. Cl.** ..... **G03g 5/04**

[58] **Field of Search** ..... 96/1.5, 1.8; 117/98 R, 117/124 E; 252/501



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[57] **ABSTRACT**

An electrophotographic charge image transfer plate, of the type comprising a matrix of interconnected photoconductive crystals bound into a glass binder to form a porous photoconductive charge transfer layer bonded to an underlying electrically conductive photon transparent substrate, has its charge transfer characteristics stabilized by infiltrating an electrically insulative material into the porous surface of the photoconductive layer. The infiltrated insulative material coats the interior surfaces of the porous glass coated and bound layer with a coating of the insulative material, whereby the charge transfer characteristics of the charge transfer plate are stabilized.


**8 Claims, 4 Drawing Figures**

FIG. 1

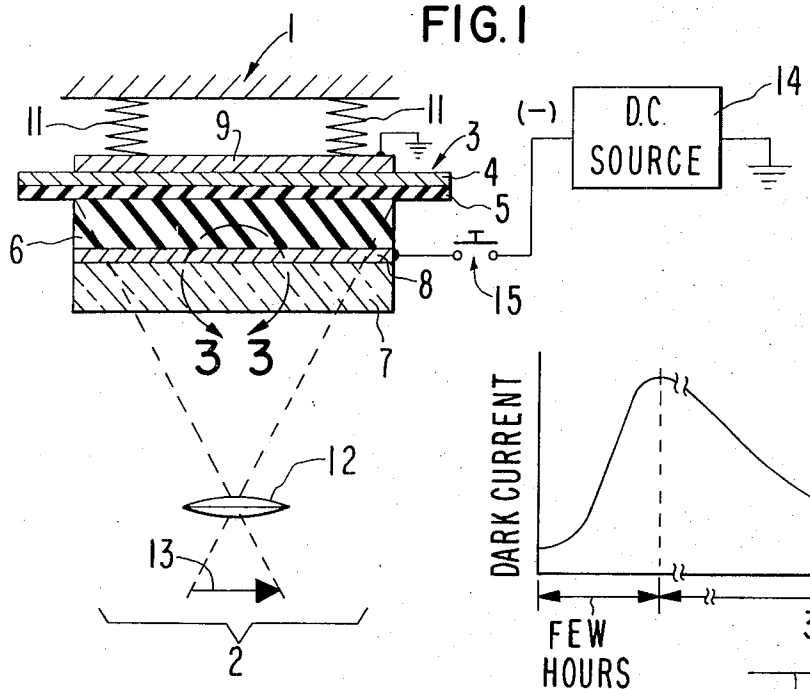



FIG. 2

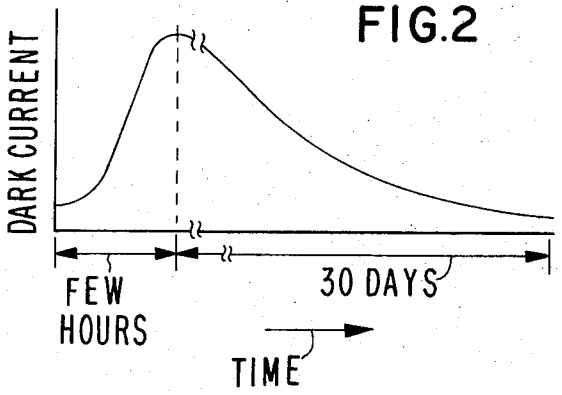



FIG. 3

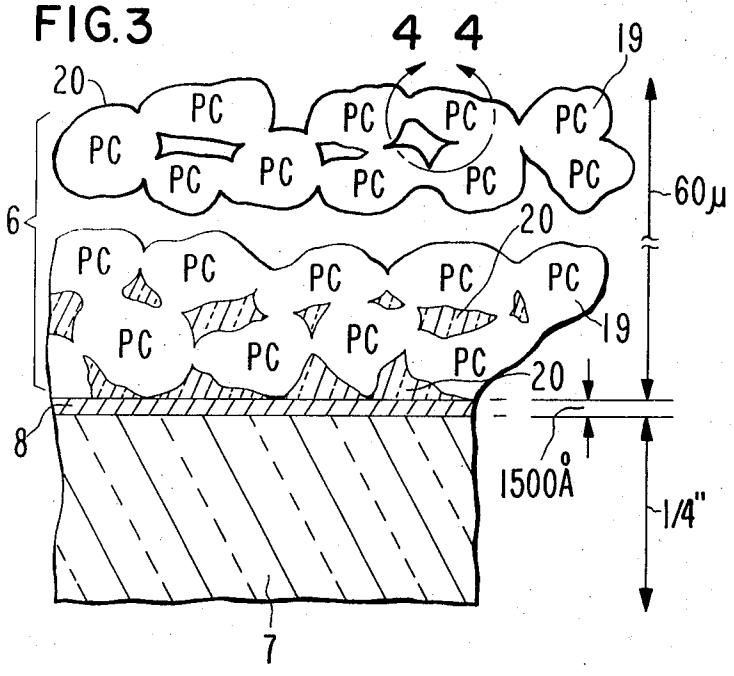
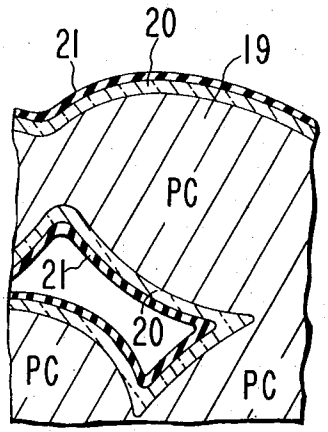



FIG. 4




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# PHOTOCONDUCTOR-GLASS BINDER PLATE WITH INSULATING RESIN IN PORES

This is a continuation of application Ser. No. 131,385 filed Apr. 5, 1971.

## DESCRIPTION OF THE PRIOR ART

Heretofore, electrophotographic charge image transfer plates of the type comprising an interconnecting matrix of photoconductive crystals, such as cadmium sulfide, coated with glass and bound by the glass into a porous photoconductive charge transfer layer overlaying an electrically conductive photon transparent substrate, have been stabilized with regard to dark current by aging for approximately 30 days in air. These plates are used in an electrophotographic mode wherein a charge image is transferred through the image illuminated plate to an electrographic recording medium, such as conductive paper having a thin dielectric charge image retentive film supported thereon.

These powders are mixed together in a volatile vehicle to form a paint or paste which is applied to an electrically conductive coated glass substrate. The assembly is fired in air at a temperature sufficient to melt the glass and to produce sintering of the photoconductive crystals. Upon cooling to room temperature, the photoconductive crystals recrystallize and due to the preponderance of photoconductive material the photoconductive materials grow together where they touch each other to form an interconnected matrix of photoconductive material which is bound together by and coated with the glass.

The resultant photoconductive charge transfer member is relatively porous having an exposed surface portion which is approximately 20 percent void and 80 percent solid material. Such electrophotographic charge transfer plates and methods for making same are disclosed and claimed in co-pending U.S. application Ser. No. 721,331 filed Apr. 15, 1968 and assigned to the same assignee as the present invention.

It has been found that electrophotographic charge image transfer plates of the aforedescribed type, on being removed from the furnace, exhibit a relatively low dark current. Dark current is the current that will flow through the photoconductive member in the absence of illumination with a given electrical potential applied across the photoconductive member. Dark current is undesired because it results in transferring undesired charge to the background area of the charge image transferred to the electrographic recording web. However, after a few hours out of the furnace and with exposure to the atmosphere, the dark current characteristic of the photoconductor has substantially increased to an unacceptable level. Upon further aging, such as for 30 days in air or for a lesser time in an over at 70°C, the dark current characteristic decreases with time such that after approximately 30 days the dark current has been reduced to an acceptable level. It is desired to provide an improved electrophotographic charge image transfer plate which does not require aging and which has improved resistance to damage to the charge transfer characteristics due to handling, humidity, temperature and exposure to a bright light.

In the art of xerography, xerographic plates have been employed which comprise photoconductive crystals suspended in a glass binder. In these plate a preponderance of glass is provided such that the individual photoconductive crystals are not interconnected to form a photoconductive matrix. In addition these xerographic plates, due to the large percentage of glass, do not have a porous surface. In fact, special care is taken to assure that the photoconductive layer of the xerographic plate has a glossy or smooth non-porous surface. Such prior art xerographic plates are disclosed in U.S. Pat. No. 3,151,982 issued Oct. 6, 1964.

Plates of this type have been rendered more abrasive and humidity-resistant by overcoating the smooth exposed surface of the plate with a relatively thin coating of epoxy, such epoxy coating being within the range of 0.1 to 5 microns in thickness. Such a xerographic plate is disclosed in Canadian Pat. No. 818,387 issued July 22, 1969.



## SUMMARY OF THE PRESENT INVENTION

The principal object of the present invention is the provision of an improved electrophotographic charge transfer plate and method of making same.

In one feature of the present invention, the porous exposed surface of a glass and photoconductor matrix type electrophotographic charge transfer plate is infiltrated with an electrically insulative material to coat the interior glass coated surfaces of the porous layer, with a coating of the insulative material, whereby the charge transfer characteristics of the charge transfer plate are stabilized.

In another feature of the present invention, the material which is infiltrated into the pores of the plate comprises an organic insulative material dispersed in a volatile liquid vehicle.

In another feature of the present invention, the organic material which is infiltrated into the pores of the photoconductive layer is selected from the class consisting of acrylic resins, ethyl cellulose and vinyl resins.

In another feature of the present invention, the insulative material is infiltrated into the pores of the photoconductive layer by spraying a liquid volatile vehicle carrying the organic insulative material therein onto the exposed porous surface of the layer.

In another feature of the present invention, the insulative material is infiltrated into the pores of the layer by spraying the organic material onto the exposed surface of the porous layer and then washing the organic material from the surface into the pores of the layer with a liquid volatile solvent for the organic material.

In another feature of the present invention, a polymerizable organic liquid or combination of liquids is infiltrated into the pores of the photoconductive layer and polymerized in situ.

Other features and advantages of the present invention will become apparent upon a perusal of the following specification taken in connection with the accompanying drawings, wherein:

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic cross-sectional view, partly in block diagram form, of an electrophotographic apparatus incorporating features of the present invention.

FIG. 2 is a plot of dark current vs time depicting the aging of a photoconductive charge transfer member of the prior art.

FIG. 3 is an enlarged detail view of a portion of the structure of FIG. 1 delineated by line 3—3 and,

FIG. 4 is an enlarged detail view of a portion of the structure of FIG. 3 delineated by line 4—4.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to FIG. 1, there is shown an electrophotographic printer 1 incorporating features of the present invention. The electrophotographic printer 1 includes an electrophotographic station 2.

The electrographic recording web 3 from a supply roll not shown comprises a conductive paper backing 4 having a thin film of dielectric material 5 supported thereon and forming the charge retentive surface. In a typical example, the conductive paper backing 4 has a bulk resistivity of approximately $10^8$ ohm-centimeters and the dielectric film 5 has a typical thickness of 4 microns. Such electrographic recording paper 3 is commercially available from Plastic Coating Corporation of Holyoke, Massachusetts and from Consolidated Paper Company of Wisconsin Rapids, Wisconsin. This type of electrographic recording web, its use, and the advantages thereof are disclosed in the aforecited U.S. Pat. No. 3,502,408.

In the electrophotographic station 2, the electrographic recording web 3 is positioned with the charge retentive surface 5 facing a photoconductive plate member 6 which is supported upon a photon transmissive substrate 7, as of glass. A photon transparent electrode 8, as of tin oxide 1500 A thick, is deposited on the transparent substrate 7 intermediate the substrate 7 and the photoconductor 6 for applying an electrical potential across the photoconductor 6. A conductive backing plate 9 overlays the conductive side 4 of the electrographic recording web 3 and is pressed into nominal physical contact with the web 3 for sandwiching the web 3 between the photoconductor 6 and the conductive plate 9. Springs 11 spring bias the plate 9 into engagement with the conductive side 4 of the electrographic recording web 3.

A projection lens 12 projects an image 13, such as that produced by an illuminated strip of microfilm, onto the photoconductor 6. A source of dc potential 14, as of −400 to −1000 volts is applied between the electrode 8 and the backing plate 9 and thus across the photoconductor 6 and the electrographic recording web 3, by means of a timer switch 15 which applies the potential to the electrode 8 for a pre-determined exposure time.

The photoconductor 6 is rendered conductive in accordance with the pattern of photon illumination projected thereon by the projection lens 12. The applied potential, supplied from source 14 via switch 15, transfers a charge image corresponding to the photon image 13 onto the charge retentive surface 5 of the electrographic recording web 3. The charge image is subsequently developed by a toning station, not shown, by application of either dry or liquid electrographic toner to the image bearing side of the electrographic recording web 3.

The quality of the printed electrographic image depends upon the charge transfer characteristics of the electrophotographic charge transfer member 6 (photoconductor 6). A particularly suitable photoconductor 6 comprises a matrix of interlocking and interconnected photoconductive crystals coated and bound together with a low melting point glass, such as solder glass, interstitially disposed in the interlocking photoconductive matrix.

The method for making such a photoconductive charge transfer member 6 is disclosed and claimed in the aforecited U.S. Pat. application Ser. No. 721,331. Briefly, the method comprises the steps of forming a layer on the conductively coated substrate 7 of a mixture of particles of glass and photoconductive crystals selected from the class consisting of sulfides, tellurides, selenides and sulfoselenides of a member of the group consisting of zinc and cadmium. Such photoconductive crystal particles are generally of the size of several microns in diameter.

The photoconductive crystal particles may be preactivated with suitable activator material, such as halides and compounds of copper or silver, or the activator may be incorporated with the powdered mixture, e.g., as cadmium chloride, to provide the halide and copper chloride to provide the metal activator. A suitable flux for the photoconductor includes halides of cadmium of zinc. Suitable glasses include the lead sealing glasses having a softening temperature between 50° and 250°C below the temperature at which the mixed particles are heated for melting the flux. Glass particles preferably comprise between 5 and 40 percent by weight of the total mixture of glass, fusing agent or flux, activator and photoconductor.

The powdered mixture may be added to a quantity of ethyl alcohol and xylene forming a volatile vehicle such that the mixture may be sprayed or applied as a paste over the transparent conductive electrode 8 on the substrate 7. The coating is applied to a thickness of approximately 20 to 100 microns and the coated assembly is placed in a furnace operating in air at approximately 500°-600°C for 15 to 60 minutes and then allowed to cool to room temperature.

The resultant photoconductive charge tansfer member 6 has a consistency as shown in FIGS. 3 and 4. More specifically, the photoconductive layer 6 comprises an interlocking matrix of photoconductive crystals 19 coated and bound together with sealing glass 20 which is interstitially disposed in the interlocking crystal matrix. The individual photoconductive crystal particles are sintered to each other so that a photoconductive bridge is formed between adjacent touching photoconductive crystals. The preponderance of photoconductive crystals assures the existence of the photoconductive bridges between the particles. The sealing glass 20 coats the fused photoconductive crystal particles and provides a bond for bonding the matrix of interlocking photoconductive crystals to the electrically conductive substrate 7.

The photoconductive layer 6 comprises between 5 and 40 percent by weight of glass with a particularly desirable proportion of glass being between 15 and 30 percent of the total weight of the layer 6. The exposed surface of the photoconductive layer 6 is relatively porous having by volume approximately 20 percent voids and 80 percent solids.

Referring now to FIG. 2, there is shown the dark current characteristics vs time for the photoconductive layer 6, after it has been withdrawn from the sintering furnace. More particularly, immediately after withdrawing the photoconductive layer from the furnace and allowing it to cool to room temperature, the dark current, i.e., the current that will flow through the conductor in the absence of light with a given electrical po-

tential difference applied across the photoconductor, is at an acceptably low level.

Dark current should be minimized as it contributes to undesired background in the electrophotographic charge image transferred to the recording medium **3.** However, upon exposure to the atmosphere for a few hours, the dark current characteristic of the photoconductive layer increases rapidly to an unacceptably high level. Upon further exposure to the atmosphere, such as for 30 days, the dark current characteristic substantially decreases back to an acceptable level. Therefore, in the prior art, the photoconductive plates have been aged for approximately 30 days in air at room temperature for stabilizing the dark current. Alternatively, the aging process can be expedited by heating the photoconductive member in an oven at approximately 70° C for several days.

It has been found that the dark current characteristics, as well as other characteristics of the photoconductor, such as sensitivity to humidity, fingerprints, handling, temperature and exposure to bright light, can be stabilized by infiltrating an electrically insulative material into the pores of the photoconductive layer **6** to coat the interior surface of the porous layer, with a coating of the insulative material.

More particularly, it has been found that certain organic insulative materials, such as acrylic resins, ethyl cellulose, and vinyl resins, when infiltrated into the pores of the photoconductive layer form the thin insulative coating **21** (See FIG. **4**). This coating **21** on the glass coating substantially stabilizes the dark current at an acceptably low level stabilizes stabilizer other charge transfer characteristics of the layer **6** rendering same relatively insensitive to humidity, temperature, handling, and exposure to bright light.

The insulative layer **21,** overlaying the outside surface of the photoconductor **6** should be relatively thin, i.e., less than 1 micron in thickness, in order such as not to interfere with proper charge transfer from the photoconductive layer **6** to the adjacent charge retentive surface **5,** of the recording medium **3.**

In a preferred embodiment the matte or dull appearance of the photoconductive layer **6,** after infiltration of the insulative material, is preferably retained in order to assure a certain microscopic surface roughness to produce a very minute air gap, as of 10 microns or less, between the charge retentive surface **5** of the recording web **3** and the exposed upper surface of the photoconductive layer **6.** This surface roughness facilitates obtaining the best quality in the developed electrographic images.

The precise mechanism by which the insulative coating **21** reduces the dark current to an acceptable level and thus avoids the aging process, and how it serves to stabilize the other charge transfer characteristics of the photoconductive layer **6** is not fully understood.

The insulative material can be infiltrated into the porous layer **6** by spraying a sufficiently dilute solution of the insulative material in a volatile vehicle onto the surface or by spraying a less dilute solution of the insulative material onto the porous surface and then washing off the excess insulative material with a liquid volatile solvent for the insulative material.

In one example a suitable spray material applied by an automatic spray booth includes **5** grams of Hercules N-22 ethyl cellulose mixed with 25 milliliters of N-hexanol, 50 milliliters of toluene and 25 milliliters of xylene. This mixture is then sprayed onto the surface and is sufficiently dilute to infiltrate the pores of the photoconductive layer **6.** Thereupon the volatile solvents are driven off leaving a thin coating of the ethyl cellulose throughout the porous layer.

In a second example of a suitable material to be sprayed onto the layer in an automatic spray booth, 7 to 10 percent by weight of DuPont Elvacite 2046 acrylic resin is dissolved in xylene, then sprayed onto the surface of the photoconductor.

In a third example, Krylon brand crystal clear acrylic resin available in aerosol spray form and manufactured by Krylon, Inc. of Norris-town, Pa. is sprayed onto the exposed porous surface of the photoconductive layer **6.** The spraying is immediately followed by washing the spray with a solvent for the spray, namely, acetone. The acetone serves to wash off the excess spray to provide a thin coating throughout. If the arcylic aerosol spray is sufficiently dilute the step of washing after spraying is not required.

In a fourth example Vikem brand clear vinyl protective aerosol spray manufactured by Bel-Art Products of Pequannock, New Jersey, is sprayed and washed, as aforedescribed for the Krylon acrylic resin, into the pores of the photoconductive layer **6.**

In another method of infiltrating the porous photoconductor layer, a polymerizable organic liquid system impregnates the pores and then is polymerized or condensed in situ. As an example, methyl methacrylate monomer is combined with 0.5 percent benzoyl peroxide as a catalyst and infiltrated into the porous photoconductive layer. The excess of liquid is wiped off, and a thin sheet of polyethylene terephthalate is placed in contact with the photoconductive layer in order to keep away air which inhibits the polymerization. A glass plate is placed over the polyethylene terephthalate, and the sandwich is placed into an oven at 50℃ to speed the polymerization. Optionally, some polymerized acrylic resin may be dissolved in the methyl methacrylate monomer before infiltration.

In another example of the formation of a resin layer in situ, a two-component unfilled epoxy resin system is mixed just before infiltration into the photoconductor pores, and then cured. Since such systems are fairly viscous the infiltration may be aided by coating the plate with epoxy, placing it in a vacuum chamber, releasing the vacuum, then mixing or scraping off the excess resin.

What is claimed is:

**1.** A method for stabilizing the charge image transfer characteristics of an electrophotographic charge image transfer member of the type comprising a matrix of inorganic photoconductive crystals in a glass binder in which the glass comprises between about 5 to about 40 percent by weight of the photoconductive layer and in which the photoconductive layer is overlying and bound to an electrically conductive substrate, such photoconductive layer being porous and having an exposed surface with a matte appearance, comprising processing as follows:

infiltrating pores in communication with the external surface of said photoconductive layer with an electrically insulative organic resin selected from the group consisting of acrylics, epoxy, ethyl cellulose, and vinyls by applying such a resin to the external surface; and,

removing any excess resin from said surface so that such resin applied to said photoconductive layer is on average less than about 1 micron thick at said exposed surface,

the external surface of the photoconductive layer having pores connunicating with pores in said layer after such processing.

**2.** The method of claim **1** in which said resin is applied by spraying in a volatile liquid vehicle.

**3.** The method of claim **2** in which the insulating organic resin comprises an acrylic resin.

**4.** The method of claim **3** in which excess resin is removed by washing with a solvent for said acrylic resin.

**5.** An electrophotographic charge image transfer member comprising:

photon transparent electrically conductive substrate means;

an inorganic photoconductive layer overlaying the substrate means and being bonded thereto;

the photoconductive layer comprising a matrix of inorganic photoconductive crystals in a glass binder, the glass comprising between about 5 to about 40 percent by weight of the photoconductive layer;

the photoconductive layer being porous and having an external surface adapted to be disposed facing and in nominal contact with a dielectric charge retentive layer of an electrographic recording web for transfer of the charge image to the charge retentive layer in response to illumination by a photon image and simultaneous application of a charge transfer potential across the charge image transfer member and the web;

pores of said photoconductive layer in communication with said external surface having infiltrated therein an insulative organic resin for stabilizing the charge image transfer characteristics of the charge image transfer member, such resin in said photoconductive layer being on average less than about 1 micron thick at said external surface; and

said external surface having pores communicating with pores in said layer.

**6.** The electrophotographic charge image transfer member of claim **5,** wherein the insulative organic material is a resin selected from the group consisting of acrylic, epoxy, ethyl cellulose, and vinyl resin.

**7.** The electrophotographic charge image transfer member of claim **5,** in which the photoconductive crystals comprise cadmium sulfide.

**8.** The electrophotographic charge image transfer member of claim **5,** in which the resin comprises an acrylic resin.

* * * * *

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# UNITED STATES PATENT OFFICE
# CERTIFICATE OF CORRECTION

Patent No. 3,830,648 Dated August 20, 1974

Inventor(s) Sherman L. Rutherford and Morris Feinieib (sic)

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

The name of the second inventor should be spelled as follows: "MORRIS FEINLEIB".

Signed and sealed this 19th day of November 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents