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ELECTROSTATIC PRINTING

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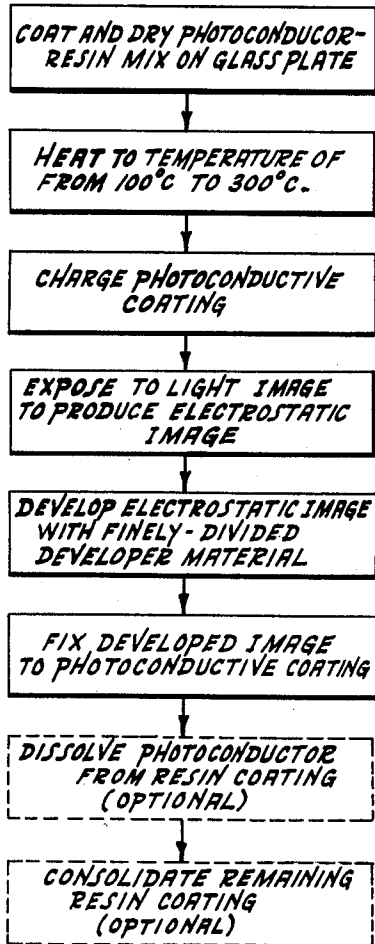
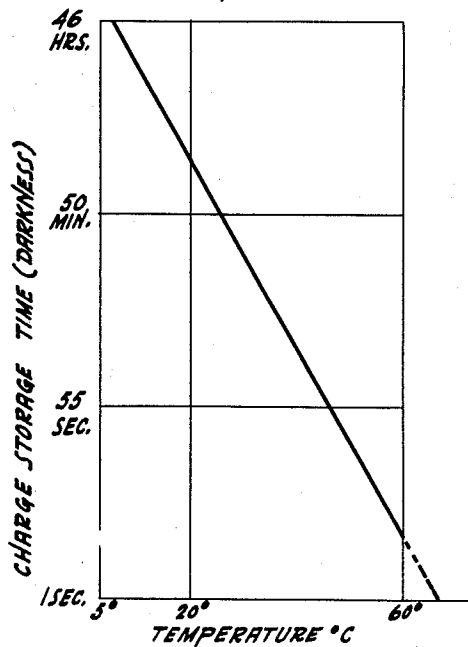
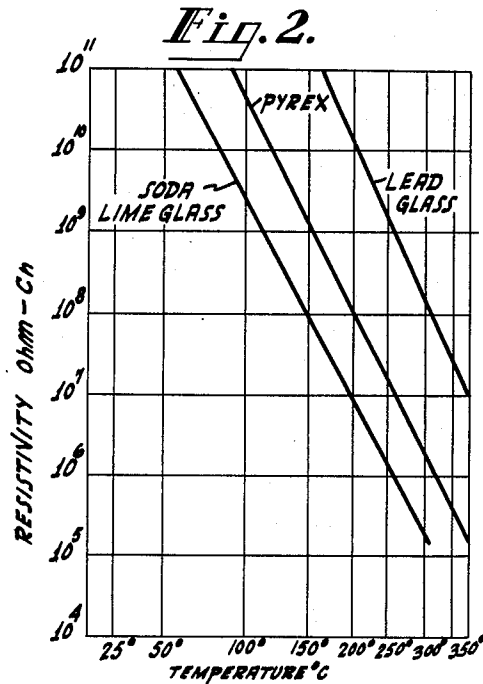


Fig. 1.

Fig. 3.



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ELECTROSTATIC PRINTING

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This invention relates to electrostatic printing and, more particularly, but not exclusively, to the production of visible images on glass employing electrostatic printing procedures.

A typical electrostatic printing process may include coating a backing with a photoconductive insulating material and then producing on the coating a latent electrostatic image. Such an image may be rendered visible by applying thereto a finely-divided developer substance such as a pigmented thermoplastic resin powder which is electrostatically held on the surface in configuration with the latent electrostatic image. The visible powder image thus formed may be then fixed directly on the coating or it may be transferred to another surface and fixed thereon.

Methods are known whereby electrostatic printing procedures are employed to produce visible images on glass. One such method, relating to the preparation of lantern slides, includes coating the surface of the glass with a conductive film such as by evaporating thereon a layer of tin chloride. Superimposed on this conductive layer is a layer of photoconductive material. The conductive layer is grounded and the photoconductive layer charged as by being subjected to a corona discharge. A light image is then focused upon the photoconductive layer to produce therein a latent electrostatic image. This image is then developed with a finely-divided developer substance and the developer substance fixed to the photoconductive layer.

In another method, a conductive plate is coated with a photoconductive material, the coating charged, exposed to a light image to produce a latent electrostatic image, and this image is then developed with a finely-divided developer substance. The developed image is then transferred by contact or other means to the glass surface on which it is fixed to provide the visible image on the glass.

Certain disadvantages are inherent in any of the prior art methods for producing visible images on glass. Coating glass with a conductive material such as tin chloride is relatively expensive. In addition, it is rather difficult to apply a ground connection to such a coating. Any method involving transfer of powder images from one surface to another results in a certain loss of image detail and is therefore unsatisfactory for many applications. These difficulties cannot be easily overcome because of the fact that most glasses, conventionally employed have too high a volume resistivity to permit a photoconductive coating thereon to be electrostatically charged. Such glasses have a resistivity greater than 10^{10} ohms cms., whereas in electrostatic printing a photoconductive coating requires a backing having a volume resistivity of 10^{10} ohm cms. or less.

Accordingly, it is a general object of this invention to provide improved methods for producing visible images on glass surfaces employing electrostatic printing procedures.

It is another object of this invention to provide improved methods for producing visible images on glass,

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which methods obviate the need for employing a conductive coating on the glass surface.

It is yet another object of the invention to provide an improved method for producing visible images on glass which eliminate the step of transferring a powder image from a photoconductive surface to the glass surface.

It is still another object of this invention to provide improved methods for producing lantern slides by electrostatic printing procedures.

The foregoing objects and other advantages are accomplished in accordance with the methods of this invention as follows. A glass surface is provided with a coating of photoconductive material. The coated glass is then heated to a temperature of from about 100 to 300° C.

Next the glass is electrically grounded, and during the time its temperature is returning to ambient a substantially uniform electrostatic charge is applied to the coating of photoconductive material. Upon exposure to a light image, the electrostatic charge in all areas of the coating struck by light is substantially reduced to provide a latent electrostatic image. A finely-divided developer material is then applied to the coating. The developer material is electrostatically held on the coating in substantial configuration with the latent electrostatic image.

When fixed to the coating, the developer material provides a permanent visible image thereon.

Other objects and advantages are more fully described in the following detailed description when read in conjunction with the accompanying drawings wherein:

Figure 1 is a flow chart illustrating the steps of a specific embodiment of this invention.

Figure 2 is a graph depicting the change in volume resistivity of various types of glass with increasing temperature.

Figure 3 is a graph depicting the decrease in charge storage time in a photoconductive coating with increasing temperature.

The methods of this invention are particularly adapted to the preparation of glass lantern slides. Almost any glass material may be used having a volume resistivity less than about 10^{17} ohm cms. at room temperature. A specific example is a soda-lime glass, called lantern slide B glass, which has a volume resistivity of about 10^{12} to 10^{13} ohm cms. In accordance with this embodiment, as illustrated in Fig. 1, a photoconductive coating is applied to one surface of a glass slide. Such a photoconductive coating may be prepared as follows:

Example 1

A mixture is prepared of the following materials:

65 grams of a 60% solution of resinous polysiloxane dissolved in xylene, such as GE SR-82 marketed by the General Electric Co., Silicone Products Division, Watford, N.Y.

200 grams toluene

100 grams photoconductive white zinc oxide

The zinc oxide selected should have a surface photoconductivity of at least 10^{-9} ohm⁻¹/square/watt/cm.² to light within the spectral range to which it is sensitive. This mixture is ball milled for about three hours and then applied to the surface of the glass slide. The coated glass slide is then heated until the coating thereon is dried.

The photoconductive coating applied to the glass slide will determine the spectral response, the speed of response and the contrast characteristic of the coated slide. By proper choice of the photoconductor and its binder, almost any spectral response, speed of response, or contrast may be obtained. Almost any powdered photoconductor having a sufficiently high value of surface photoconductivity may be used in the photoconductive coating; for example, the photoconductive oxides, sulfides, sele-

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nides, tellurides, and iodides of cadmium, antimony, bismuth, thallium, molybdenum, lead or zinc. It is preferable for the photoconductor to have a high electrical resistivity in the darkness. Such a photoconductor should have a volume resistivity of at least about 10^{12} ohm-cm. in darkness and upon exposure to light of appropriate wavelength a volume resistivity of about 10^{10} ohm-cm. or less. Mixtures of one or more photoconductors may be used. Photoconductors should be selected which do not melt, sublime, or decompose at temperatures to which the glass slide is to be heated.

The electrically insulating binder material is an essential part of the composition and may comprise any one of a number of substances, most desirable is a vehicle having a high dielectric strength. The binder may be any material such as a synthetic resin or wax. For example, resinous polysiloxane, cellulose ester, polystyrene, or shellac. Mixtures including one or more vehicles may be used. In the selection of a binder material it is important that it shall neither sublime nor decompose at the temperature to which the glass slide is to be heated.

The photoconductor may be suspended in the vehicle in any one of several ways. The simplest way is to dissolve the vehicle in an organic solvent capable of effecting solution and then mixing in the powdered photoconductor. Alternatively, the photoconductor may be dry blended as by kneading with the vehicle heated to a sufficiently high temperature to render it plastic.

The proportion of powdered photoconductor to vehicle in the final coating may vary over a wide range. The preferred ranges are 50% to 90% of photoconductor with, correspondingly, 50% to 10% of binder. The optimum proportions will depend on the nature of the photoconductor, the nature of the vehicle and the results desired.

The speed of response of the printing base particularly depends upon the nature of the photoconductive material, the nature of the binder material, and the ratio by weight of photoconductor to binder. Since the speed of response depends on a number of characteristics, almost any desired response may be obtained by the proper selection of materials and compositions. A proper selection of materials and compositions will also determine how long an electrostatic image may be stored on the surface of the photoconductive coating since storage of the electrostatic image depends upon the electrical resistivity of the material. Generally the higher the resistivity of the coating the longer the storage time.

The next step, in accordance with this invention, is to heat the coated glass slide to a temperature within a range of from 100° C. to 300° C. A preferred temperature is about 160° C. Once the glass plate has reached the desired temperature, it is immediately positioned upon a grounded conductive plate and subjected to a corona discharge. The corona discharge is applied across the coating on the glass until the glass plate locks down to the grounded conductive plate. By this is meant that the glass plate can only be moved on the grounded conductive plate by the application thereto of considerably more force than would be required prior to the charging of the photoconductive coating.

It is in the combination of the heating step and the charging step that a unique feature of this invention becomes apparent. Once the glass plate has become locked to the conductive backing plate, it is capable of retaining its electrostatic charge so that it may, in subsequent steps, be processed to provide thereon a visible powder image.

Although the operation of this invention is not too well understood, it is believed that the following brief description will facilitate an understanding thereof. Referring now to the graph of Figure 2, which depicts the change in volume resistivity for various types of glass including a soda-lime glass. It can be seen from the graph that a temperature approaching 100° C. is required to reduce the resistivity of the soda-lime glass to 10^{10} ohm

cms. or less as required for electrostatic printing. Higher temperatures decrease the resistivity of the glass to a greater extent until, as shown on the graph, the resistivity of the glass is less than 2×10^7 ohm cms. at temperatures above 200° C.

In Figure 3, there is shown the charge storage characteristics of a photoconductive zinc oxide coating. At temperatures approximating room temperature the zinc oxide coating is capable of retaining its electrostatic charge for at least 50 minutes. The time during which it is capable of retaining this charge decreases with increasing temperatures until at a temperature of 60° C., or above, the charge storage time amounts only to a matter of a few seconds.

A comparison of the graphs of Figures 1 and 2 shows that it is very unexpected that a coated glass slide could be heated to temperatures sufficient to provide the required conductivity in the glass without destroying completely the charge storage capability of the photoconductive coating. It is believed that what happens is the following. When the temperature of the glass is raised, for example, to 160° C., then removed from the heat source and positioned on a grounded conductive plate, both the glass slide and the coating thereon begin to cool. The glass slide cools from the bottom upward and the coating from the top down. A very thin layer of the surface of the coating becomes cool enough (60° C. or less) to retain an electrostatic charge, before the remainder of the coating and the glass slide drop below a temperature at which the resistivity of the glass exceeds 10^{10} ohm-cm. Thus, during the time that the corona charging unit is passed over the coating, a substantially uniform electrostatic charge is deposited on the surface of the photoconductive coating.

The next step comprises producing a latent electrostatic image on the photoconductive coating. This is easily accomplished by projecting a light image onto the coating as by exposure from a projector containing a photographic negative. The light image is focused on the charged surface of the photoconductive coating and wherever the light strikes the surface, the electrostatic charge thereon is removed or reduced. The electrostatic image comprises a pattern of charges which correspond to the dark portions of the projected image. Other methods of producing an electrostatic image, such as by contact exposure, may also be used.

The electrostatic image may be stored for a time if desired but ordinarily the next step is to develop the electrostatic image with a finely-divided electroscopic material. Development may be accomplished by maintaining the glass slide in darkness and passing a developer brush containing a developer powder across the photoconductive coating bearing the electrostatic image. The developer powder deposits on those areas retaining an electrostatic charge. The developer brush comprises a mixture of magnetic carrier particles, for example, powdered iron and the developer powder. A more detailed description of this method of development is contained in U.S. Patent 2,857,271 to M. L. Sugarman.

Development may also be carried out by immersing the glass slide in a liquid developer dispersion. Such a dispersion comprises an insulating carrier liquid having dispersed therein developer powder particles comprising finely-divided electrostatically-attractable material. When the glass slide is immersed in such a liquid, developer particles migrate toward the charged areas of the photoconductive coating and deposit thereon in configuration with the electrostatic image. Liquid development methods are more fully described in an article entitled "Zerography," by K. A. Metcalfe and R. J. Wright, published in the Journal of the Oil and Colour Chemists Association, vol. 39, No. 11 of November 1956, pages 845 to 862, London, England.

Once an image has been developed, as described above, the next step is to fix the image to the photoconductive

coating. If the developer powder or the binder in the photoconductive coating has a relatively low melting point, the image may be fixed by heating, for example, with a radiant heater, infra red radiation or by placing it in an oven. In this way the developer powder can be fused to the photoconductive coating to provide a permanent image. Sulfur or synthetic thermoplastic resins may be fixed in this way. Alternatively, the powder may be fixed onto the coating by means of a light application of a liquid which is either a solvent for the developer powder or for the binder material in the photoconductive coating. Such a solvent will soften its solute and cause the developer powder to adhere to the coating.

When it is desired to improve the transparency of those portions of the photoconductive coating not covered by the fixed image, this may be done by immersing the coating in a solvent solution to dissolve out the photoconductor. Where photoconductive zinc oxide is employed in the photoconductive coating such a solution may comprise:

	Parts by volume
Glacial acetic acid	1
Water	5
Ethyl alcohol	4
Tergitol 8	0.1

The photoconductive coating is permitted to remain in the solution with occasional agitation until the background areas become completely clear of the photoconductor. This ordinarily takes about 10 to 20 minutes. However, the time will depend upon the nature of the clearing solution with respect to the photoconductive coating and the thickness of the photoconductive coating.

The proportion of reagents in the clearing solution may be varied widely. Similarly, other reagents may be substituted for the specific reagents of the example. For instance the solvent for the photoconductor may be replaced with hydrochloric acid, sodium hydroxide, or phosphoric acid. Any reagent which will penetrate the binder and dissolve out or react with the photoconductor to form a soluble product may be used.

The proportion of the solvent in the clearing solution may be varied between 0.1% and 100%. Too low a concentration results in excessive clearing times. Too high a concentration will cause excessive bubble formation and possible rupture of the binder film.

After clearing, the cleared coating is washed thoroughly with water, dried, and heated at about 200° C. for about one hour to cure and flow the resinous polysiloxane. Before curing, the resinous polysiloxane appears translucent to transparent but after curing it is transparent with improved transmissive properties. The methods of dissolving out the photoconductor and curing the binder are more fully described in the patent of M. L. Sugarman, Jr., op. cit.

There have been described improved methods for producing visible powder images on glass surfaces. Although particularly adapted to the preparation of lantern slides, this invention is not limited solely thereto. It can be employed in any field wherein permanent visible images are desired on either flat or curved glass surfaces. Such images may also be produced on the surface of materials other than glass provided only that such materials have properties such as those described herein with respect to glass.

What is claimed is:

1. A method of electrostatic printing utilizing a substrate having a volume resistivity greater than 10^{10} ohm-cm. at about room temperature and a volume resistivity less than 10^{10} ohm-cm. at a temperature substantially within a range of about 100° C. to 300° C. and having on one surface thereof an insulating photoconductive coating, said method comprising heating said substrate to at least said temperature at which said vol-

ume resistivity is less than 10^{10} ohm-cm., substantially immediately thereafter simultaneously contacting an electrode to the uncoated side of said substrate and applying an electric field through said coating and said substrate to produce a substantially uniform electrostatic charge on said coating, discharging the charge on said coating in selected areas to produce thereon a latent electrostatic image, and developing said electrostatic image with an electroscopic developer substance to produce a visible image on said coating.

2. The method of claim 1 wherein said substrate comprises a soda-lime glass having a volume resistivity at room temperature of about 10^{12} to 10^{13} ohm-cm. and wherein said substrate is heated to a temperature of from 150° C. to 200° C.

3. A method of electrostatic printing utilizing a glass plate having a volume resistivity at room temperature of from 10^{12} to 10^{17} ohm-cm. and having on one side thereof a coating of finely-divided photoconductive insulating material dispersed in an electrically-insulating binder, said method comprising heating said plate to a temperature of from 150° C. to 250° C., substantially immediately thereafter positioning said plate on an electrically conducting surface coated side up and applying an electric field through said coating and said plate to cause said plate to become electrostatically locked to said conducting surface and to produce a substantially uniform electrostatic charge upon said coating, exposing said plate to a light image to produce a latent electrostatic image on said coating, and developing said electrostatic image with a finely-divided electroscopic material to produce a visible image on said coating.

4. The method of claim 3 wherein said plate is soda-lime glass having a volume resistivity of about 10^{12} to 10^{13} ohm-cm. and wherein said plate is heated to a temperature of from 150° C. to 200° C.

5. A method of preparing a lantern slide utilizing a glass slide having a volume resistivity within a range of from 10^{12} to 10^{17} ohm-cm., said slide having on at least one surface a coating of a photoconductive material comprising photoconductive zinc oxide dispersed in an electrically-insulating binder, said method comprising heating said slide to a temperature of from 100° C. to 300° C. to reduce the volume resistivity thereof to a value less than 10^{10} ohm-cm., substantially immediately thereafter positioning said slide on a grounded conductive plate and passing an ion-producing corona discharge over said coating on said slide until said slide becomes locked to said conductive plate thereby to produce on said coating a substantially uniform electrostatic charge, exposing said slide to a light image to produce thereon a latent electrostatic image on said coating, and applying a finely-divided developer material to said coating to produce thereon a visible image of said developer material.

6. The method of claim 5 wherein said glass slide comprises soda-lime glass having a volume resistivity of the order of 10^{12} to 10^{13} ohm-cm. and said temperature is of the order of 150° C. to 250° C.

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