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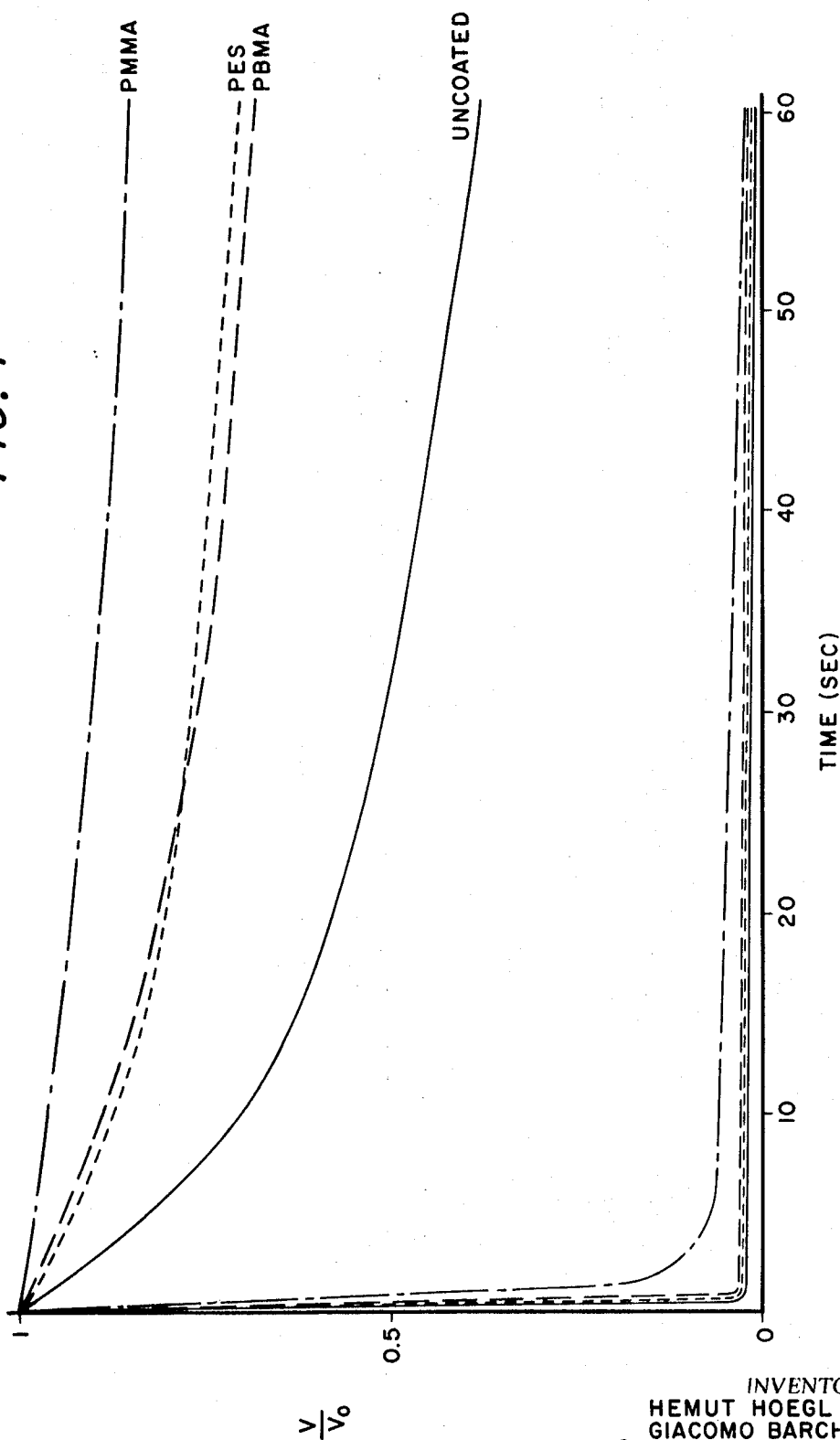
[54] **ELECTROPHOTOGRAPHIC PLATE AND PROCESS**
5 Claims, 3 Drawing Figs.
[52] U.S. Cl. **96/1.5,**
96/1, 117/201, 117/212, 117/218
[51] Int. Cl. **G03g 5/04,**
G03g 13/22
[50] Field of Search..... **96/1.5, 1.6;**
252/501; 117/201, 212, 218

[56]		References Cited	
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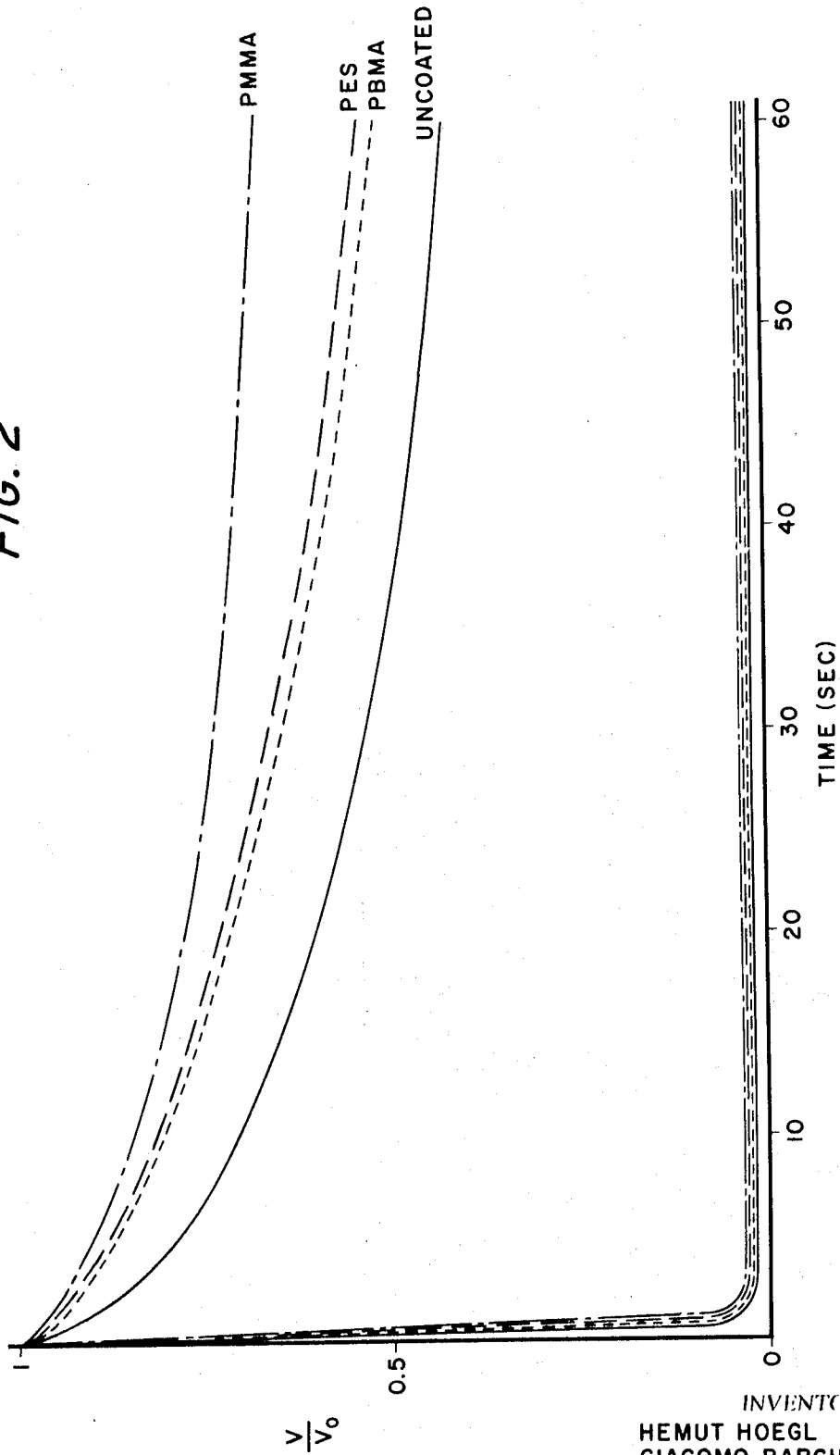
ABSTRACT: A photoconductive plate comprising a photoconductive charge transfer complex composition overcoated with a thin layer of an insulating material, preferably less than one micron thick, is disclosed. The use of this photoconductive plate in an electrostatic imaging capacity is further disclosed.

FIG. 1



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FIG. 2



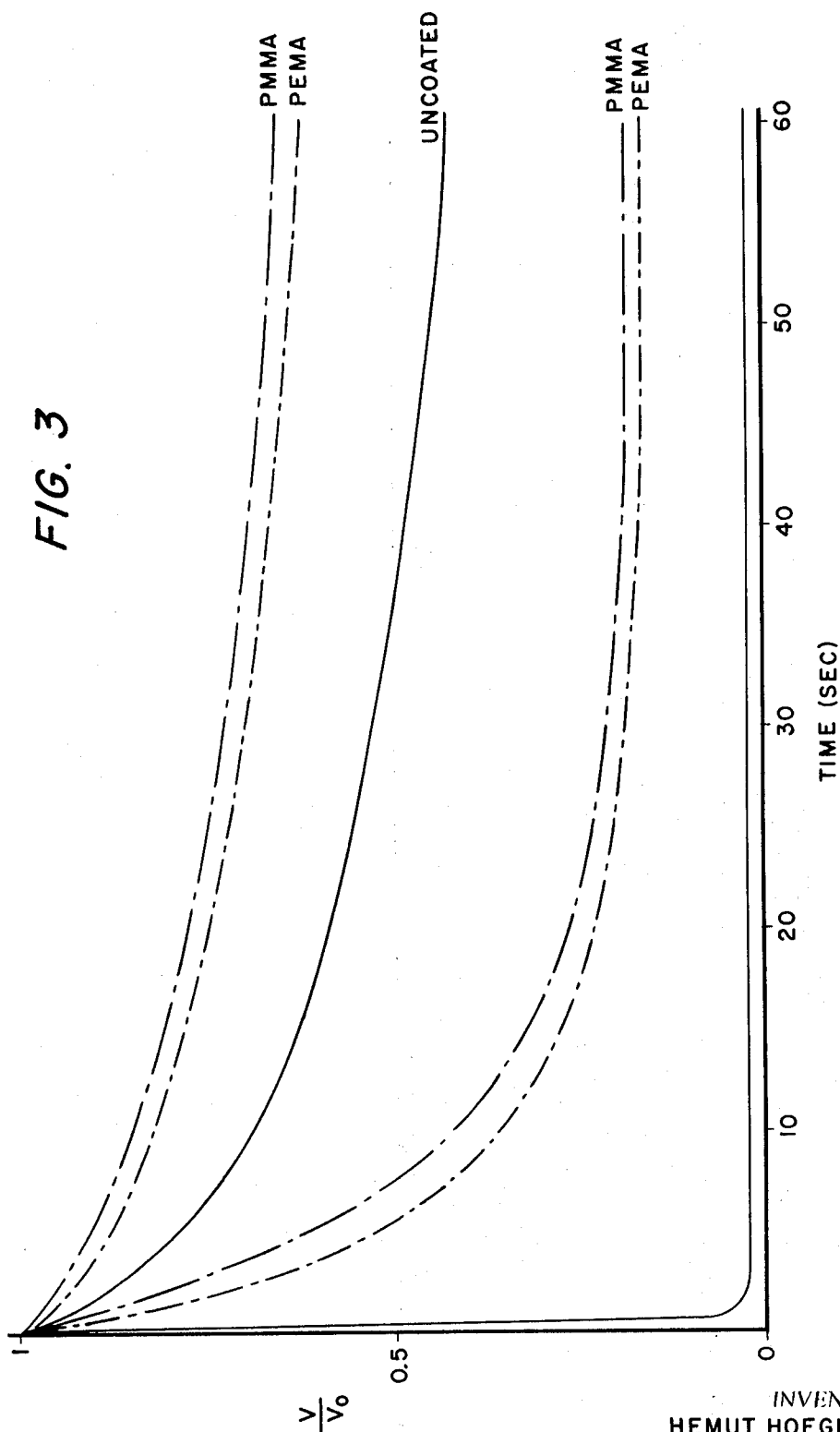
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FIG. 3



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ELECTROPHOTOGRAPHIC PLATE AND PROCESS

This invention relates in general to electrophotographic imaging processes. More specifically, the invention concerns improved electrophotographic plates for use in such imaging systems.

The fundamental electrophotographic imaging process is described by C. F. Carlson in U.S. Pat. No. 2,297,691. In this process, a base sheet of relatively low electrical resistance, such as metal, paper, etc., having a photoconductive insulating surface coated thereon, is electrostatically charged in the dark. The charged coating is then exposed to a light image. The charges leak off rapidly to the base sheet in proportion to the intensity of light to which the particular area is exposed, the charge being substantially retained in nonexposed areas, forming an electrostatic latent image. After exposure, the coating is contacted with electroscope marking particles. These particles adhere to the areas where the electrostatic charge remains, forming a powder image corresponding to the electrostatic latent image. Where the base sheet is relatively inexpensive, such as paper, the image may be fixed directly to the plate, as by heat or solvent fusing. Alternatively, the powder image may be transferred to a sheet of transfer material, such as paper, and fixed thereon. Variations on the above general process are detailed in U.S. Pat. Nos. 2,357,809, 2,891,011 and 3,079,342.

Many different photoconductive insulating materials are known for use in electrophotographic plates. Suitable photoconductive insulating materials such as anthracene, sulfur, selenium or mixtures thereof have been disclosed by Carlson in U.S. Pat. No. 2,297,691. These materials generally are sensitive only to blue or near ultraviolet and all but selenium are further limited by being only slightly light sensitive. Vitreous selenium, however, while desirable in most aspects, has a spectral response limited to the green, blue, and near ultraviolet regions of the spectrum. Also, the procedures for preparing layers of vitreous selenium are costly and complex. More recently, it has been found that certain inorganic photoconductive pigments when dispersed in suitable binder materials form useful photoconductive insulating layers. In another type plate, photoconductive organic polymers are used; frequently in combination with sensitizing dyes to form the photoconductive insulating layer. While these materials are often inexpensive and simple to prepare, their electrical photosensitivity is in general much less than that of selenium.

It has recently been found that the electrical photosensitivity of various inherently photoconductive organic materials can be increased by doping them with Lewis Acids, thereby forming charge-transfer complexes. Still more recently, it has been found that certain nonphotoconductive organic polymers form highly photosensitive charge-transfer complexes when doped with Lewis Acids. Examples of photoconductive charge-transfer complexes produced by mixing two nonphotoconductive materials are further described in detail in copending applications, Ser. No. 426,409 and 426,401, both filed Jan. 18, 1965, and now U.S. Pat. Nos. 3,408,183, and 3,408,181 respectively. While these photoconductors may be prepared by simple processes utilizing noncomplex equipment, from inexpensive materials, they in general have the drawback of relatively high dark decay. Dark decay is a measure of dissipation of an electrostatic charge while the plate is maintained in the dark. Where a high proportion of Lewis Acid is used, the plate will be highly photosensitive. However, such a plate would have such a high rate of discharge in the dark as to be unuseable in conventional imaging systems. Even where the proportion of Lewis Acid is lower, the dark decay may be so rapid as to require that the plate be charged, aged and developed in very rapid succession to produce useful images. It is necessary in conventional imaging that a plate hold a high electrostatic charge in the dark with little leakage and then quickly dissipate the charge when exposed to light.

Conventional electrophotographic imaging systems are, in general, incapable of producing images having good solid area

coverage. A large black area on an original is imaged as a black edge around a blank center. Where printing or writing is to be reproduced, this characteristic is unimportant. But where photographs or diagrams having large solid areas are to be copied, poor results are generally obtained. A great many methods of improving solid area coverage have been proposed. These may use special, complex developing processes and apparatus, half-tone screens placed on the original, special developers, etc. While these systems usually improve solid-area coverage, they are undesirably complex, often degrade the quality of line copy, and do not produce ideal solid area coverage. Thus, there is a continuing need for a simple, inexpensive method of electrophotographically copying solid image areas.

It is, therefore, an object of this invention to provide an electrophotographic plate overcoming the above-noted deficiencies.

It is another object of this invention to provide an electrophotographic plate having high electrical photosensitivity and low dark decay characteristics.

It is another object of this invention to provide an electrophotographic plate which may be prepared from inexpensive materials by noncomplex procedures.

It is still another object of this invention to provide an electrophotographic plate having spectral sensitivity in ranges of those other than prior plates.

It is still another object of this invention to provide an organic electrophotographic plate having a tough, abrasion resistant surface.

It is still another object of this invention to provide an electrophotographic plate capable of producing high quality copies of broad solid image areas.

It is yet another object of this invention to provide a method of preparing an electrophotographic plate capable of copying broad solid image areas.

It is yet another object of this invention to provide a method for preparing an electrophotographic plate having high electrical photosensitivity and low dark decay characteristics.

It is a still further object of this invention to provide a method for protecting the surface of an organic electrophotographic plate without adversely effecting its photosensitivity.

The foregoing objects and others are accomplished in accordance with this invention, fundamentally, by providing an electrophotographic plate which comprises a photoconductive layer comprising a polymer and a Lewis Acid and a thin coating on said layer of an insulating organic material. The coating may be formed as discrete, small, closely spaced dots, so as to produce a plate capable of copying broad, solid image areas.

The photoconductive layer may be coated on a relatively conductive substance such as metal, paper, etc. Alternatively, the photoconductive layer may be in the form of a self-supporting film. The polymer which is mixed with the Lewis Acid to form the photoconductive layer may be a photoconductive polymer or may be a nonphotoconductive polymer such as those described in the above-mentioned copending applications. The overcoating insulating material should be in the form of a relatively thin coating so as to not adversely effect the sensitivity of the electrophotographic plate. It has been found that the highest photoconductivity results with an overcoating layer of up to 1 micron; therefore, the preferred thickness is up to 1 micron.

Ordinarily, when a photoconductive material is overcoated with an insulator, the photosensitivity of the resulting plate is adversely effected, since the charge on the insulating overcoating is not immediately dissipated when the plate is exposed to a light image. Often, a residual charge remains on said overcoating even after intense light exposure. In the present case, surprisingly, the very thin (0-1 micron) overcoating has the effect of greatly reducing the dark decay characteristics of the organic photoconductor without adversely affecting the light discharge characteristics. The effect of the overcoating on the photosensitivity and dark decay

characteristics of an organic photoconductive plate will be further understood upon references to the examples and drawings, as further discussed below.

The thin insulating overcoating may be either a continuous film or a discontinuous film made up of closely spaced dots of the insulating material. Where the film is continuous, the resulting plate is capable of producing excellent reproductions of printing, writing and other line copy. However, when an image having broad solid areas is reproduced on such a plate, the usual "fringing" effect occurs, resulting in development of only the edge of the solid area. But, if the insulating layer is applied in the form of discrete dots, the charge on the uncoated areas between the dots will decay (due to the high dark decay rate of the uncoated plate material) even in the solid image areas. Thus, each of the dots in the solid image area will be individually developed, resulting in solid area coverage having a "halftone" appearance. Although this modification is superior for reproducing images having broad solid image areas, the plate having a continuous insulating coating may be preferred for line copy work, since the plate having the dot pattern will impose a "halftone" like pattern on the image, very slightly degrading the quality of line copy.

Any suitable organic polymer may be mixed with a Lewis Acid to form the photoconductive charge transfer complex to be overcoated forming the plate of this invention. Polyvinylcarbazole, formaldehyde polymers, polycarbonates, polystyrenes, epoxy resins, phenoxy resins, polyurethanes and mixtures and copolymers thereof, have been found to produce especially desirable results and, therefore, are preferred. Any other suitable polymer may be used where desired.

Any suitable Lewis Acid may be utilized with the above-mentioned polymers to form photoconductive charge-transfer complexes. In fact, where suitable, Lewis bases may be mixed with suitable electron-acceptor resins to form photoconductive charge-transfer complexes. As Lewis Acids, 2,4,7-trinitro-9-fluorenone and P-chloranil have been found to produce especially sensitive photoconductive charge-transfer complexes and, therefore, are preferred. Any other suitable Lewis Acid may be used as desired. Typical Lewis Acids include 9-dicyanomethylene-2,4,7-trinitro-fluorenone, 4,4-bis-(dimethylamino)-benzophenone, tetrachlorophthalic anhydride, picric acid, benzanthracene-7,12-dione, 1,3,5-trinitro-benzene, 2,5-dichlorobenzoquinone, 4-nitrobenzaldehyde, maleic anhydride, 2-acetyl-naphthalene, phthalic acid and mixtures thereof.

The overcoating may comprise any suitable insulating material. Polymethylmethacrylate, polymethylacrylate, poly-n-butylmethacrylate and polyethylsilicate have been found to produce tough, thin, insulating coatings over the above-mentioned polymer-Lewis Acid mixtures, and, therefore, are preferred. Any other suitable insulating material may be used, if desired. Typical insulating materials are chlorinated rubber, vinyl polymers, polyolefins, vinylidene polymers, fluorocarbon polymers, polyamides, polyesters, polyurethanes, polysulfides, polycarbonates and mixtures thereof. The thin overcoating layers on the resin-Lewis Acid charge-transfer complex layer may be formed by any suitable method. Glow discharge polymerization such as is described in detail by Goodman in U.S. Pat. No. 2,932,591 has been found to be an especially desirable method. In this process, the photoconductive layer is exposed to a gaseous polymerizable dielectric film-forming substance while an electric field is maintained in the region of said surface to cause a glow discharge to said surface. This forms on said surface a solid, continuous polymerized homogeneous dielectric film of high resistivity. Thus, a smooth, tough coherent film having the desired thickness, e.g., 0-1 micron, is formed. Where it is desired to form a discontinuous film, the insulating material is applied to the photoconductive layer through a screen. Since the field used in glow discharge polymerization directs the depositing ions in a straight line through the screen, very high resolution can be attained. For example, resolution on the order of 150 line pairs per millimeter may be maintained with the screen spaced about 1/4 inch from the plate surface.

Where it is desired to form a discontinuous thin insulating layer on the photoconductor, any suitable means may be used. A sieve made up of metallic wires held adjacent the plate during coating is typical. The screen should have a fine mesh, so that the uncoated spaces between coated areas are small. A conventional sieve of 50 to 100 mesh gives desirable results.

The effect and advantages of the thin overcoating on a photoconductive layer may further be understood by reference to the drawing, wherein:

FIG. 1 presents a graphic analysis of the electrical characteristics of plates tested in examples I-IV below;

FIG. 2 presents a similar graphical analysis of the tests of examples V-VIII; and,

FIG. 3 presents a similar analysis of the control tests of examples IX-XI.

Referring now to the figures, there are seen graphs having two sets of curves. Here, the ordinate is the ratio of the charge measured on the plate (V) at a given time to the original charge imposed on the plate (V_0). The abscissa is time in seconds. The upper series of lines represent plate discharge in the dark (dark decay) and the lower set of lines represent discharge upon light exposure. Ideally, dark discharge will be very slow and these lines would slope very little. Light discharge should be very rapid to a very low value. In each of FIGS. 1-3 the solid line represents uncoated plates, as tested in examples I, V and IX; the "PMMA" lines represent the polymethylmethacrylate overcoated plates as tested in examples II, VI and X; the "PBMA" lines represent the poly-n-butylmethacrylate overcoated plates as tested in examples III and VII; the "PES" lines represent the polyethylsilicate overcoated plates as tested in examples IV and VIII and the "PEMA" lines represent the polyethylmethacrylate overcoated plates as tested in example XI. As can be seen from the figures, the 0.5 micron overcoatings greatly improve the dark discharge characteristics of the plate without adversely affecting their light discharge characteristics. The curves of FIG. 3, which compare on overcoated plates to plates having a 3 micron overcoating show that the thicker overcoatings are undesirable since they adversely affect photosensitivity by increasing residual potential after light exposure.

The following examples further specifically define the present invention with respect to the use of thin insulating overcoatings over photoconductive charge-transfer complex layers to reduce dark decay without adversely affecting photosensitivity. Parts and percentages are by weight unless otherwise indicated. The examples below are intended to illustrate various preferred embodiments of the electrophotographic plate of this invention. Dark and light discharge characteristics are measured in a conventional manner, using a Feedback Electrostatic Voltmeter, Model 107-AS -4, manufactured by Monroe Electronic Inc., Middleport, New York.

EXAMPLE I

Initially, an electrophotographic plate is prepared as follows. A solution is prepared of equal volumes of toluene and tetrahydrofuran. In this solvent mixture is dissolved equal parts by weight of polyvinyl carbazole and 2,4,7-trinitro-9-fluorenone until a 12 percent solution is attained. Aluminum sheets are dip coated from this solution until a layer having a thickness of about 7 microns is obtained.

This plate is charged in the dark to a potential of about 800 volts by means of conventional corona charging means such as is described in U.S. Pat. No. 2,777,957. The plate is maintained in the dark and the charge remaining on the plate is continuously measured for sixty seconds and plotted in FIG. 1. The plate is then recharged to a potential of about 800 volts and exposed to white light of about 8.3 mw. intensity. The change in the ratio of retained potential to initial potential with respect to time is again plotted in FIG. 1. As can be seen from FIG. 1, the dark discharge of the unovercoated photoconductive charge transfer layer is relatively rapid. Light discharge of this nonovercoated layer is very rapid

showing high photosensitivity. The curves for the nonovercoated charge transfer complex can be used as a standard against which the overcoated charge transfer layers can be compared.

EXAMPLE II

An electrophotographic plate is initially prepared as in example I above. The plate is then overcoated with a 0.5 micron layer of polymethylmethacrylate by the process described in U.S. Pat. No. 2,932,591. The monomer used is methylmethacrylate, stabilized with 10 percent hydroquinone, available from Fluka A. G. Buchs, Switzerland. The glow discharge is maintained for about 15 minutes at about 300 kHz. The current intensity used is about 30 milliamps, peak-to-peak, with a starting pressure of about 2.8×10^{-11} mm. mercury. An electrode having a surface of about 145 cm.² is used at a distance of about 70 millimeters from the plate to be coated. About 50 cm.² of the sample is coated simultaneously.

The overcoated plate is then charged in the dark to a potential of about 800 volts. While the plate is maintained in the dark, continuous measurements of potential retained are made and plotted in FIG. 1. The plate is then recharged to about 800 volts and exposed to a white light. The light discharge characteristics of this plate are similarly measured and indicated in FIG. 1.

EXAMPLE III

An electrophotographic plate is initially prepared as in example I above. The plate is then overcoated with about a 0.5 micron layer of poly-n-butylmethacrylate by the method used in example II. The monomer is n-butylmethacrylate available from Fluka A.G. Operating conditions are the same as in example II except that the glow discharge is maintained for 10 minutes at a current intensity of about 60 milliamps and a starting pressure of about 3×10^{-11} millimeters of mercury. This plate is charged to a potential of about 800 volts and the dark decay characteristics are plotted in FIG. 1 as with the above examples. The plate is then recharged to a potential of about 800 volts and exposed to white light. The light discharge characteristics are similarly plotted.

EXAMPLE IV

An electrophotographic plate is initially prepared as in example I above. The plate is then overcoated with about 0.5 micron layer of polyethylsilicate by the process described in example II. The monomer used is ethylsilicate, available from Fluka A. G. Glow discharge conditions are the same as in example III above. The plate is charged to a potential of about 800 volts in the dark and the dark discharge characteristics are measured and plotted as in FIG. 1. The plate is then recharged to about 800 volts and exposed to a white light. The light discharge characteristics are similarly plotted in FIG. 1.

EXAMPLE V

An electrophotographic plate is initially prepared as follows. A solvent mixture comprising equal parts by volume of toluene and tetrahydrofuran is prepared. About 10 parts polyvinyl carbazole and about 1 part *p*-chloranil are dissolved in this solvent until about a 7 percent solution is attained. An aluminum plate is dip-coated with this solution until a layer having a thickness of about 7 microns is obtained.

This charge-transfer complex plate is charged in the dark to an initial potential of about 400 volts. Residual potential on the plate is continuously measured in the dark for about 60 seconds. The dark discharge characteristics of the plate are plotted in FIG. 2. As can be seen from FIG. 2, the uncoated plate has relatively high dark discharge. The plate is then recharged to a potential of about 400 volts and then exposed to a white light of an intensity of about 8 microwatts. As can be seen from FIG. 2, this plate is highly photosensitive, e.g. the charge is dissipated very rapidly upon exposure to light. The

two curves for this plate can be used as a control against which the corresponding curves for uncoated plates can be compared.

EXAMPLE VI

An electrophotographic plate is initially prepared as in example V above. This plate is then overcoated with about a 0.5 micron of polymethylmethacrylate by glow discharge polymerization under the conditions given in example II above.

The overcoated plate is charged to an initial potential of about 400 volts in the dark. The dark decay characteristics of the plate are measured and the results plotted as in FIG. 2. The plate is then recharged to a potential of about 400 volts and exposed to white light. The light discharge characteristics are then similarly plotted in FIG. 2.

EXAMPLE VII

An electrophotographic plate is prepared as in example V above. This plate is then overcoated with about a 0.5 micron layer of poly-n-butylmethacrylate by glow discharge polymerization under the conditions described in example III above.

The overcoated plate is then charged in the dark to a potential of about 400 volts. The dark discharge characteristics of this plate are measured and plotted in FIG. 2. The plate is then recharged to a potential of about 400 volts and exposed to a white light. The light discharge characteristics of the plate are then similarly plotted in FIG. 2.

EXAMPLE VIII

An electrophotographic plate is prepared as described in example V above. The plate is then overcoated with about a 0.5 micron layer of polyethylsilicate by glow discharge polymerization under the conditions described in example IV above.

The plate is initially charge to a potential of about 400 volts in the dark. The dark discharge characteristics of the plate are measured and the results plotted in FIG. 2. The plate is then recharged to a potential of about 400 volts and the plate is exposed to a white light. The light discharge characteristics of the plate are then similarly plotted.

EXAMPLE IX

An electrophotographic plate is initially prepared as in example I above. This unovercoated plate is charged in the dark to a potential of about 500 volts. The dark discharge characteristics of this plate are measured and the results plotted in FIG. 3. The plate is then recharged to a potential of about 500 volts. The plate is exposed to a white light of about 8.3 mw. intensity. The light discharge characteristics are then measured and plotted. As can be seen from FIG. 3, this uncoated plate has excellent light discharge characteristics but undesirable high dark discharge.

EXAMPLE X

An electrophotographic plate is prepared as described in example I above. The plate is then overcoated with about a 3 micron layer of polymethylmethacrylate by dip coating from a solution.

The plate is charged to a potential of about 500 volts and the dark discharge characteristics are measured and plotted in FIG. 3. The plate is then recharged, exposed to a white light of about 8.3 mw. intensity and the light discharge characteristics are measured and plotted. As can be seen from FIG. 3, while the relatively thick overcoating improves the dark discharge curve, it adversely affects the light discharge curve, and thus lowers the photosensitivity of the plate.

EXAMPLE XI

An electrophotographic plate is prepared as described in example I above. The plate is then overcoated with about a 3 micron layer of polyethylmethacrylate by dip coating.

The plate is charged to a potential of about 500 volts and the dark discharge characteristics are measured and plotted in FIG. 3. The plate is then recharged, exposed to a white light of about 8.3 mw. intensity and the light discharge characteristics are measured and plotted. As can be seen from FIG. 3, the relatively thick overcoating adversely affects the light discharge characteristics of the plate.

EXAMPLE XII

An electrophotographic plate is prepared and overcoated with a continuous insulating film as in example I. The plate is charged to a potential of about 800 volts and exposed to an image having both narrow lines and broad solid image areas. The electrostatic latent image is cascade developed by the method described in U.S. Pat. No. 2,618,551. An excellent reproduction of the line copy is observed, but only the edges of the broad solid areas are developed.

EXAMPLE XIII

An electrophotographic plate is prepared as described in example I above. A 100 mesh brass wire sieve is held above ¼ inch from the surface of the plate and a coating of polymethylmethacrylate is applied to the plate through the sieve by the method described in example II. An even pattern of closely spaced dots having a thickness of about 0.5 micron.

The overcoated plate is then charged in the dark to a potential of about 800 volts and exposed to an image having both narrow lines and broad solid image areas. The electrostatic latent image is cascade developed. An excellent image is observed, having toner deposited across the broad solid areas in half-tone configuration. The quality of the line copy is good, but not quite as high as that of example XII.

Although specific components and proportions have been stated in the above description of preferred embodiments of

the overcoated photoconductive charge-transfer layer, other suitable materials, as listed above, may be used with similar results. In addition, other materials may be added to the mixture to synergize, enhance, or otherwise modify its properties.

For example, dye sensitizers may be added to the photoconductive layer to broaden the spectral response of the material.

Other modifications and ramifications of the present invention will occur to those skilled in the art upon a reading of the disclosure. These are intended to be included within the scope of this invention.

What is claimed is:

1. An electrophotographic plate comprising a photoconductive charge transfer complex composition having superimposed charge transfer complex composition having superimposed on the surface thereof an insulating polymer in the pattern of spaced dots.

2. The electrophotographic plate as described in claim 1 wherein said insulating polymer has a thickness of up to about 1 micron.

3. An electrophotographic imaging process comprising:

a. forming an electrostatic latent image on the surface of a photoconductive plate said plate comprising a photoconductive charge-transfer complex composition having superimposed thereon in the form of a pattern of spaced dots a thin layer of an insulating polymer; and

b. developing said latent image with electrically attractable marking particles to produce a visible image.

4. An electrophotographic imaging process comprising uniformly charging the surface of a photoconductive plate comprising a photoconductive charge-transfer complex composition having superimposed on the surface thereof an insulating polymer in the form of a pattern of spaced dots, selectively exposing said photoconductive plate to a light source thereby producing an electrostatic latent image and developing said latent image with electrically attractable marking particles to produce a visible image.

5. The process as disclosed in claim 4 wherein said insulating polymer ranges in thickness up to about 1 micron.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,607,258 Dated September 21, 1971

Inventor(s) Helmut Hoegl and Giacomo Barchietto

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

IN THE CLAIMS:

Claim 1. Line 14, please delete "charge transfer complex composition having superimposed".

Signed and Sealed this

second Day of March 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks