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**PHOTO-ACTIVE MEMBER FOR XEROGRAPHY**  
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This invention relates in general to xerography and in particular to a sensitive plate for xerography. More specifically, the invention relates to a new xerographic electrophotographic member comprising a conductive backing having on at least one surface thereof a coating of photoactive crystalline material contained in and activating a photoconductive insulating layer.

In the art of electrophotography which is otherwise known as xerography, it is usual to form an electrostatic image on a member or plate which comprises a conductive backing member such as, for example, a metallic surface which backing member has a photoconductive insulating layer on its surface. The electrostatic image may subsequently be developed by exposure to a finely divided electrically attractable material. Heretofore it has been found that selenium has been the most satisfactory photoconductive insulating material and, therefore, prior plates have consisted of conductive backing members with coatings of vitreous selenium thereon.

Now in accordance with this invention it has been found that a xerographic or electrophotographic sensitive member can be prepared with photo-active crystals and pigment materials of a type of molecular structure rather than atomic structure, i.e. tending to break up as molecules rather than as atoms. For example, photo-active crystals of luminescent or phosphor properties generally undergo a change of energy state with incident radiation as evidenced by elevation of one or more electrons to a higher energy level wherein the electron is relatively more free to migrate as an n-type semi-conductor or wherein the electron leaves a "positive hole" to act as a p-type semi-conductor. Typical crystals and pigments possessing these properties are cadmium sulfide, zinc sulfide, lead sulfide, cadmium selenide, zinc selenide, mixed sulfides or selenides of these metals and other crystalline materials generally available under the class of phosphors, usually with activating amounts of other elements such as, for example, up to about 1% and generally about 0.001 to 0.01% of elements such as copper, zinc, calcium, silver, magnesium and the like. In particular the photo-active crystal is employed in conjunction with a photoconductive insulating material to supply activating centers for the photoconductive layer. Thus, the photo-active crystal may be employed in conjunction with a photoconductive insulator such as vitreous selenium, sulfur, anthracene or the like.

The binder material which is employed in cooperation with the photoactive crystal is a material which is an insulator to the extent that an electrostatic charge placed on the layer is not conducted in the absence of illumination at a rate to prevent the formation and retention of an electrostatic latent image thereon. In general, this means that the specific resistivity of the binder material should be at least about  $10^{13}$  ohms-cm. and preferably will be several orders higher. Within this broad range of operability the nature of the binder material will affect the image quality and the actual performance of a plate prepared therewith, but is not critical in characteristics, composition, or methods of application. For optimum results, however, it is preferred that the specific resistivity of the binder material be such that the over-all resistivity of the coating in absence of illumination be between  $10^{13}$  and  $10^{18}$  ohms-cm. In many instances a suitable binder

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may be photoconductive, and its photoconductivity may be enhanced or varied in photographic speed or in spectral range by activation by such binders. For example, amorphous or vitreous-appearing selenium, anthracene, sulfur and the like which are, themselves, photoconductors may suitably act as binders for these activating crystalline materials.

The function of the base or backing material used in preparing xerographic binder plates is to provide physical support for the photoconductive insulating layer and to act as a ground thereby permitting the photoconductive insulating layer to receive an electrostatic charge in the dark and permitting the charges to migrate when exposed to light. It is evident that a wide variety of materials may be used, for example, metal surfaces such as aluminum, brass, stainless steel, copper, nickel, zinc, etc.; conductively coated glass as tin- or indium-oxide coated glass, aluminum coated glass, etc.; similar coatings on plastic substrates; or paper rendered conductive by the inclusion of a suitable chemical therein or through conditioning in a humid atmosphere to insure the presence therein of sufficient water content to render the material conductive. To act as a ground plane as described herein, the backing material may have a surprisingly high resistivity such as  $10^6$  or  $10^8$  ohms-cm.

Where the composite layer of binder and photoactive compound has sufficient strength to form a self-supporting layer (termed "pellicle"), it is possible to eliminate a physical base or support member and substitute therefor any of the various arrangements well known in the art in place of the ground plane previously supplied by the base layer. A ground plane, in effect, provides a source of mobile charges of both polarities. The deposition on the other side of the photoconductive insulating layer (from the ground plane) of sensitizing charges of the desired polarity causes those charges in the ground plane of opposite polarity to migrate to the interface at the photoconductive insulating layer. Without this the capacity of the insulating layer by itself would be such that it could not accept enough charge to sensitize the layer to a xerographically useful potential. It is the electrostatic field between the deposited charges on one side of the photoconductive layer and the induced charges (from the ground plane) on the other side that stresses the layer so that when an electron is excited to the conduction band by a photon thereby creating a hole-electron pair, the charges migrate under the influence of this field thereby creating the latent electrostatic image. It is thus obvious that if the physical ground plane is omitted a substitute therefor may be provided by depositing on opposite sides of the photoconductive insulating pellicle simultaneously electrostatic charges of opposite polarity. Thus, if positive electrostatic charges are placed on one side of the pellicle as by corona charging as described in U.S. 2,777,957 to L. E. Walkup, the simultaneous deposition of negative charges on the other side of the pellicle also by corona charging will create an induced, that is, a virtual, ground plane within the body of the pellicle just as if the charges of opposite polarity had been supplied to the interface by being induced from an actual ground plane. Such an artificial ground plane permits the acceptance of a usable sensitizing charge and at the same time permits migration of the charges under the applied field when exposed to activating radiation. As used hereafter in the specification and claims, the term "conductive base" includes both a physical base and an "artificial" one as described herein.

The physical shape or conformation of the xerographic binder plate may be in any form whatsoever as desired by the formulator such as flat, spherical, cylindrical, etc. The plate may be flexible or rigid.

In the preparation of a xerographic or electrophoto-

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graphic plate or member according to this invention, a convenient procedure involves mixing together of the desired quantities of the photoactive material and the binder material preferably together with solvent for the binder material and painting, flowing or spraying mixture onto a suitable conductor surface such as, for example, a metallic plate in a layer between about 20 and 200 microns thick. Where, as in the case of selenium, the binder is not conveniently soluble in usual solvents, the mixture may be heated and flowed or pressed onto the surface or otherwise applied in a convenient manner to yield a uniform layer. In general, the ratio between binder and photo-active crystalline material is from about one part binder and 10 parts photo-active crystal to about 2 binder and 1 part photo-active crystal. The binder should be employed in sufficient quantity to form a smooth shiny surface, while the crystalline material should be employed in sufficient quantity to effect the desired change or improvement in photo-response of the layer. In this connection it is pointed out that the subsequent steps after the formation of the electrostatic image include production of a powder image on the surface and optionally its transfer therefrom, which steps can be performed much more satisfactorily and with results of superior quality using a smooth and preferably mirror-finished surface.

The general nature of the invention having been set forth, the following examples are now presented as illustrations but not limitations of the methods and means of carrying out the invention.

#### Example 1

10% by weight of a cadmium-zinc sulfide crystal composition available under the name Phosphor 2225 (New Jersey Zinc Company) was incorporated in substantially pure selenium and carefully ground to avoid overheating or crystallization in the grinding process. The finely ground mixture was then incorporated in a liquid adhesive binder consisting of Parlon (chlorinated rubber) and Rezyl (an alkyd resin in xylene solution). This mixture was painted on an aluminum plate surface to yield an operable xerographic plate capable of accepting an electrostatic charge and dissipating such charge upon illumination. Care was taken to paint a smooth, uniform layer, and the layer thickness was about  $\frac{1}{200}$  inch.

#### Example 2

A quantity of substantially pure selenium was melted and an equal amount of weight of a zinc-cadmium sulfide crystal composition available under the name, "Phosphor 2215," from the New Jersey Zinc Company, was dispersed in the melt by stirring. The resulting mixture was then knife-coated on a heated aluminum plate to give a uniform layer of the crystals in a binder of vitreous selenium. The resulting xerographic plate was capable of accepting an electrostatic charge and dissipating the charge on illumination.

#### Example 3

The procedure of Example 2 was followed using a zinc sulfide crystal composition available under the name, "Phosphor 2205," from the New Jersey Zinc Company. The resulting xerographic plate was capable of accepting an electrostatic charge and dissipating the charge upon illumination.

#### Example 4

The procedure of Example 2 was followed using a zinc sulfide crystal composition available under the name, "Phosphor 2310," from the New Jersey Zinc Company. The resulting xerographic plate was capable of accepting an electrostatic charge and dissipating the charge upon illumination.

#### Example 5

The procedure of Example 2 was followed using a zinc sulfide crystal composition available under the name "Phosphor 2330," from the New Jersey Zinc Company.

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The resulting xerographic plate was capable of accepting an electrostatic charge and dissipating such charge upon illumination.

#### Example 6

The procedure of Example 2 was followed using a zinc-cadmium sulfide crystal composition available under the name, "Phosphor 2304," from the New Jersey Zinc Company. The resulting xerographic plate was capable of accepting an electrostatic charge and dissipating the charge upon illumination.

#### Example 7

The procedure of Example 2 was followed using C.P. grade zinc sulfide. The resulting xerographic plate was capable of accepting an electrostatic charge and dissipating the charge upon illumination.

#### Example 8

The procedure of Example 2 was followed using a commercial grade of lead sulfide (PbS). The resulting xerographic plate was capable of accepting an electrostatic charge and dissipating the charge upon illumination.

Many other photo-active materials have been found suitable for the preparation of xerographic plates, and the following commercially available materials among others may be employed for the purpose: Phosphor 2100 (a zinc oxide phosphor material available from New Jersey Zinc Company); Phosphors 2110 and 2115 (zinc-magnesium oxide); Phosphors 2205, 2330, and 2301 (zinc sulfide); Phosphors 2215, 2220, 2225, and 2304 (zinc cadmium sulfide); Phosphors 2469 and 2479 (calcium-strontium sulfide), all available from the same source; Phosphors F-2039 (zinc cadmium sulfide), F-2032 (zinc oxide), F-2046 (zinc sulfide), all available from the Radio Corporation of America; and Phosphors 511 (zinc oxide), 601 (ZnSiO<sub>2</sub>), 1200 (zinc-cadmium sulfide) and 501 (calcium tungstate), all available from E. I. du Pont de Nemours and Company.

Instead of the selenium base binder of Example 2 there may be employed other photoconductive materials. For example, the photo-active materials listed herein may be incorporated with anthracene in an organic solvent such as alcohol, benzene, ether, or the like, and the mixture coated on a conductive surface. More desirably, however, a binder mixture containing sulfur or anthracene in place of selenium and containing an additional organic binder may be employed. For this purpose various polystyrene resins, silicone resins, acrylic and methacrylic polymers and copolymers, and other insulating plastics and resins have been found desirable and useful.

When an organic photoconductor such as anthracene is used, it is desirable to form a solid solution of the photoconductor in a suitable resin. Generally, the addition of a resin slightly reduces the photographic speed of the photoconductor; however, the increased toughness of the photoconductive film and ease of coating are generally considered to compensate for the slight loss in speed. As illustrative of the process of forming such a film which is eminently suitable for rapid coating, a saturated solution of freshly sublimed anthracene in benzene or other solvent is made up and then ethyl cellulose or other binder is added to the anthracene solution in proportions of from about one-fiftieth to one-half the weight of the anthracene, preferably about one-fifth of the weight of anthracene. The photoactive pigment particles are then added to the solution in the desired concentration and the resulting suspension applied to the backing member as by spraying, brushing, whirling, the use of a dip roll, doctor blade, etc. The solution dries rapidly and forms a smooth, adherent layer eminently suitable to the instant invention.

The xerographic members prepared according to this invention are generally comparable with or better than xerographic plates in terms of photographic or xerographic speed. Generally, they will accept an electrostatic charge of at least about 300 volts and will maintain this charge

for a half-time period of at least several minutes and in some cases at least several hours in the absence of illumination. An electroscopic or electrically attractable powder can be deposited on an electrostatic image on the surface of the members and can, if desired, be transferred to a second surface. The quality of images or pictures formed with these members is roughly comparable with images from selenium plates.

Correlation between particle size and picture quality or graininess can be observed, within somewhat broad limits. Thus, finer quality results are achieved with increasing subdivision or grinding of a particular photo-active crystal, the quality improving with more finely ground crystals until the degree of grinding has begun to impair the photoconductivity. It has been found that at the range of about 0.5 micron, additional grinding does not improve quality but, instead appears to break up the necessary crystal structure or otherwise deleteriously affects the properties of the material. For this reason particle size of between 0.5 and 5.0 and preferably about 1.0 micron is presently preferred where fineness of particle is achieved by grinding.

However, where the particle size is determined by other methods such as, for example, crystal growth, it appears that particle size should be as small as possible, preferably less than about 1 micron with the minimum size determined by the appearance of sufficiently defined crystal structure to evidence photoconductivity. It is understood and believed that the crystals employed as described in the examples, contain small quantities of impurities in the crystal structure which impurities act as activation centers. Among the impurities deemed to be satisfactory for this purpose are small quantities usually less than 1% and frequently in the range of 0.001 to 0.01% of an element such as copper, calcium, sodium, and the like, which are present in luminescent or phosphor types of photo-active crystals.

It is observed that there is a certain degree of similarity between the properties of photoconductivity as required by the present invention and phosphorescence of luminescence as possessed by the commercial phosphors. In each case it is presently believed that the desired property is imparted to the crystal by the presence of crystal imperfections which cause the presence of electrons in a reduced energy level, which electrons can by the action of light or suitable radiation be raised to a higher energy level. In the case of the photoconductive material such as is employed in the present invention, the critical requirement or property differs from that of luminescence in that the crystal is not significantly electrically conductive with the electron in the lower energy level but becomes substantially conductive with the electron in the higher energy level; presence or absence of a glow effect or luminescence is immaterial. In other words, the higher electron energy level is a conduction level. It is believed that the characteristics and activity of the photo-active pigment materials can be adequately explained by a development of this theory but it is not intended to limit the invention to this or any other theory of operation.

As is clear from the examples, the photoactive pigment materials need not be luminescent. Thus, in addition to those shown in the examples, other pigments which may be used include, but are not limited to, materials such as antimony trisulfide, indium trisulfide, mercuric sulfide, mercuric iodide, arsenic disulfide, arsenic trisulfide, arsenic triselenide, gallium triselenide, cadmium selenide, tetragonal lead monoxide, red lead oxide (minimum), mercuric oxide, zinc oxide, and titanium dioxide. The function of these pigment materials in the xerographic plates of the instant invention is not completely understood. It is believed that they serve two functions. Thus, in the xerographic process an electric field is placed across a photoconductive insulating material applying an electrostatic stress thereto. On exposure to light hole-electron pairs are created in the photoconductor. These charges move

through the photoconductor in accordance with the lines of force of the applied electrostatic field. Those charges reaching the surface of the xerographic plate act to create an electrostatic image thereon either by neutralizing charge of opposite polarity already existing thereon or, in the case of an externally applied field, by being trapped at the surface to create an electrostatic image thereon. In the plates of the instant invention the presence of the pigment in the body of the photoconductor is believed to inject charge carriers excited in the pigment into the photoconductor, thus creating an additional source of mobile charges in the photoconductor in addition to those created by the hole-electron pairs due to the action of the photons on the photoconductors.

Even more important than this mechanism is believed to be a more efficient use of the incident light. The mechanism can best be understood by considering a specific case such as, for example, that of vitreous selenium. Vitreous selenium is sensitive almost wholly to the blue and near ultraviolet. Radiation in this part of the spectrum is absorbed in the very topmost layers of the selenium exposed to the incident radiation. Radiation having a longer wavelength, particularly red light, penetrates for a considerable distance into the selenium before it is absorbed. Radiation of this wavelength does not have sufficient energy to raise an electron to the conduction band in vitreous selenium. Accordingly, its absorption adds nothing to the overall spectral sensitivity of the selenium plate. Most commercial light sources as incandescent, photoflood, and sunlight have an appreciable if not major portion of their radiation in the red and far red portions of the spectrum. In the plate prepared according to the instant invention containing a pigment or phosphor sensitive to the red or far red such as lead sulfide, gallium triselenide, indium trisulfide, mercuric sulfide, etc. the blue and ultraviolet light incident on the selenium matrix containing pigment particles of the aforesaid material is absorbed on or near the surface of the selenium creating hole-electron pairs therein. The red light penetrating to a greater depth in the selenium creates hole-electron pairs in the pigment particles as far down as the red light penetrates into the selenium. Charge carriers generated by the red light in the pigment particles in the bulk of the selenium are then injected into the selenium from the pigment particles wherein they move under the influence of the applied electrostatic field. Thus, the plate makes use of a much larger portion of the spectrum thereby increasing overall light sensitivity and considerably extending spectral response.

Xerographic plates consisting of a uniform layer of photoconductive insulating material have very strenuous electric requirements. In order to support an electrostatic charge in the dark, such a material must have a resistivity of at least about  $10^{13}$  ohms-cm. and desirably will have a resistivity of  $10^{15}$  ohms-cm. or greater. In the case of a binder plate such as described in our copending application, Serial No. 668,165, filed June 26, 1957, which consists of a photoconductive pigment in an insulating resin binder, the interpolation of multiple layers of highly insulating resin surrounding the pigment particles is sufficient in itself to support a considerable electrostatic field thereby permitting the employment as photoconductive pigment particles of pigments having substantially lower orders of electrical resistivity in the dark than is the case for xerographic films employing uniform layers of photoconductors. As the entire photoconductivity is due to the pigment particles—the resin being a photographically inert component—relatively high concentrations of pigment to binder must be used to obtain reasonable levels of light sensitivity. In general, depending upon the degree of pigment concentration and the insulating nature of the resin, the pigment must have a resistivity of at least about  $10^{10}$  ohms-cm. In the xerographic plates of the instant invention the binder itself may be the photoconductor, the pigment acting merely

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as an activator therefor. As compared to binder plates, substantially lower concentrations of pigment may be used to modify the light sensitivity of the photoconductor forming the light sensitive layer of the xerographic plate. In general, the pigment may comprise from about five percent to about eighty percent by weight of the total photoconductor composition. In general, it is preferred to employ from about five percent to about fifty percent by weight of pigment based on the total amount of photoconductor. As is evident, for the lower concentrations of pigment used, it is possible to use pigments having resistivities substantially lower than those necessary for the pigments in binder plates wherein the pigment constitutes the sole photoactive component. In general, it is believed that the pigment may have a resistivity of as low as about  $10^8$  ohms-cm.

Many variations of the instant invention will at once be obvious to those skilled in the art. Thus, if desired, the spectral response of the pigment may be further modified by the inclusion of photosensitizing dyes. Thus, a dye solution may be applied to the crystals of pigment to coat the surface thereof prior to inclusion in the photoconductive film as of selenium, anthracene, etc. One such combination would be to treat particles of zinc oxide with an alcohol solution of rose bengal dye which may then be included in a binder of amorphous selenium or anthracene. In addition to treating pigment particles with dye, particularly when organic photoconductors are used, the dye may be added to the solution of photoconductor or photoconductor and resin as is well-known to those skilled in the art. In general, the dyes useful for this purpose are those commonly used in photographic sensitization and the basic mechanism of dye sensitization in xerography is believed to be the same as that of photographic sensitization. By using such dyes singly or in combination, it is possible to further modify the resulting xerographic plate.

Regardless of theories of operation, it is observed that the electrophotographic members according to this invention have a very high specific resistivity in the absence of activating illumination, this resistivity is usually between  $10^{13}$  and  $10^{18}$  ohms-cm. and the sensitivity is caused to drop several orders of magnitude by exposure to bright light such as direct sunlight.

This application is a continuation-in-part of our application S.N. 311,546, filed September 25, 1952, and now abandoned.

We claim:

1. The method comprising applying an electric field through a two-phase layer of photoconductive insulating material comprising a uniform homogeneous photoconductive insulating material having dispersed therein from about 5 to about 50% by weight of a particulate inorganic photoconductive crystalline pigment thereby forming a chemically distinct phase in said homogeneous photoconductive insulating material and projecting an image onto said layer whereby a flow of electricity takes place through said layer by generation of charge carriers in said homogeneous photoconductive insulating material and by injection of charge carriers from said photoconductive crystalline pigment into said homogeneous photoconductive insulating material whereby the light sensitivity of the layer is increased producing an electrostatic image at a surface thereof, said electrostatic image being developed by electroscopic marking particles.

2. The method according to claim 1 wherein said

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electrostatic image is rendered visible by applying electrostatically charged marking particles to said surface.

3. The method according to claim 1 wherein the homogeneous photoconductive insulating material is vitreous selenium.

4. The method according to claim 1 wherein the homogeneous photoconductive insulating material is an organic photoconductive insulating material.

5. The method according to claim 4 wherein the photoconductive crystalline pigment is selected from the group consisting of the sulfides and selenides of cadmium, zinc and lead, antimony trisulfide, indium trisulfide, mercuric sulfide, mercuric iodide, arsenic trisulfide, arsenic disulfide, arsenic triselenide, gallium triselenide, tetragonal lead monoxide, minium, mercuric oxide, zinc oxide and titanium dioxide.

6. The method according to claim 1 wherein the homogeneous photoconductive insulating material consists essentially of a solid solution of an organic photoconductive material in from about  $\frac{1}{50}$  to about  $\frac{1}{2}$  the weight of the organic photoconductive material of an organic resinous binder therefor.

7. The method according to claim 6 wherein the organic photoconductive material is anthracene.

8. The method according to claim 6 wherein the photoconductive crystalline pigment is selected from the group consisting of the sulfides and selenides of cadmium, zinc and lead, antimony trisulfide, indium trisulfide, mercuric sulfide, mercuric iodide, arsenic trisulfide, arsenic disulfide, arsenic triselenide, gallium triselenide, tetragonal lead monoxide, minium, mercuric oxide, zinc oxide and titanium dioxide.

9. The method according to claim 8 wherein the crystalline pigment is a zinc-cadmium sulfide.

10. The method according to claim 8 wherein the crystalline pigment is a zinc-cadmium selenide.

11. The method according to claim 8 wherein the crystalline pigment is a zinc sulfide.

12. The method according to claim 8 wherein the crystalline pigment is a cadmium selenide.

13. The method according to claim 8 wherein the crystalline pigment is a zinc selenide.

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