

Oct. 9, 1973

J. MORT ET AL

3,764,315

AMBIPOLAR ELECTROPHOTOGRAPHIC PLATE

Filed July 24, 1972

6 Sheets-Sheet 1

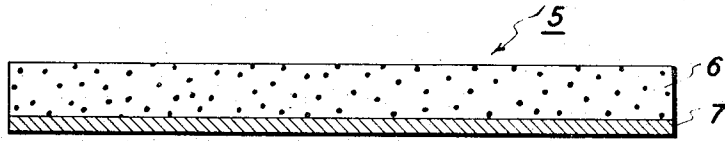


FIG. 1

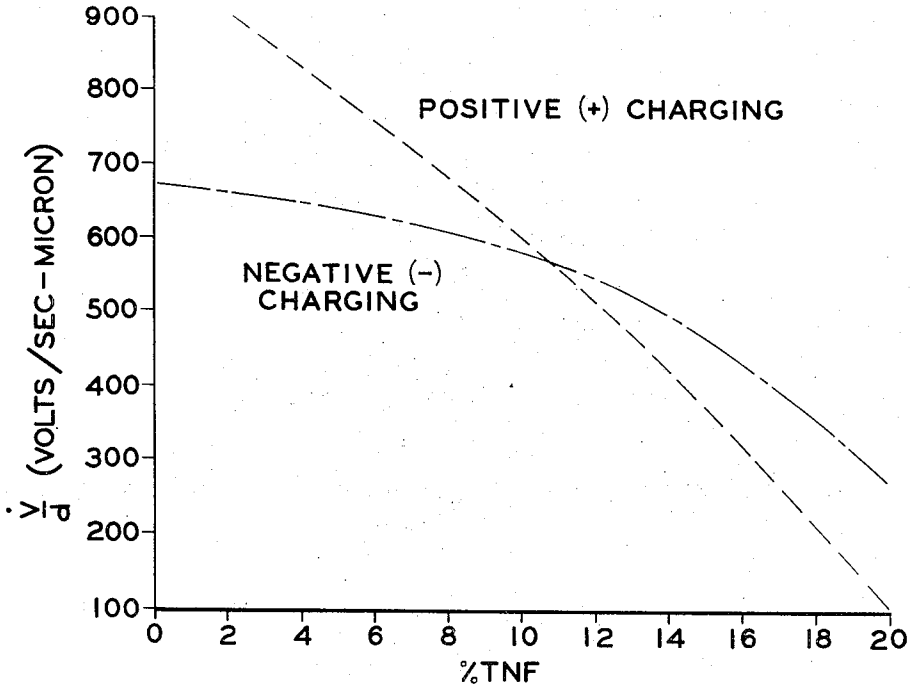


FIG. 2

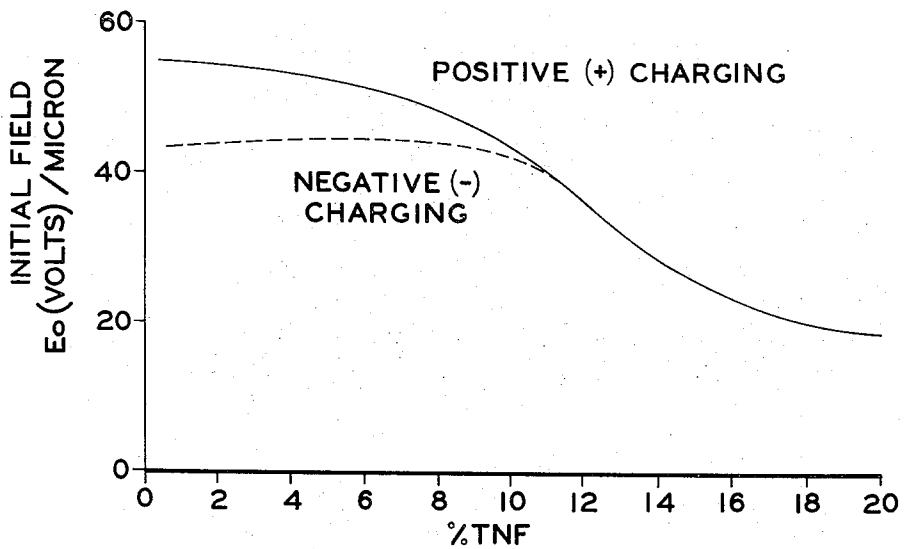


FIG. 3

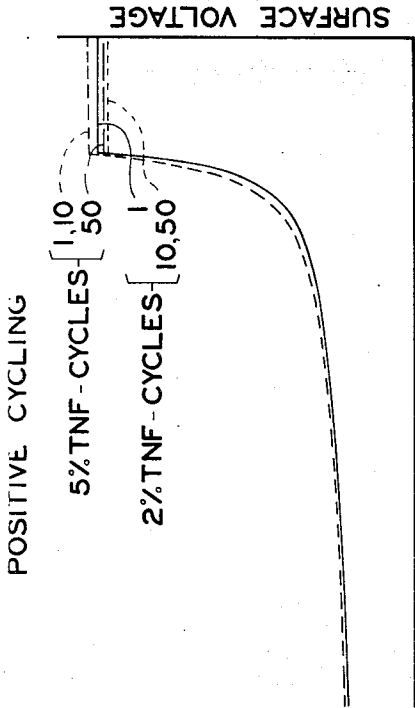


FIG. 4b

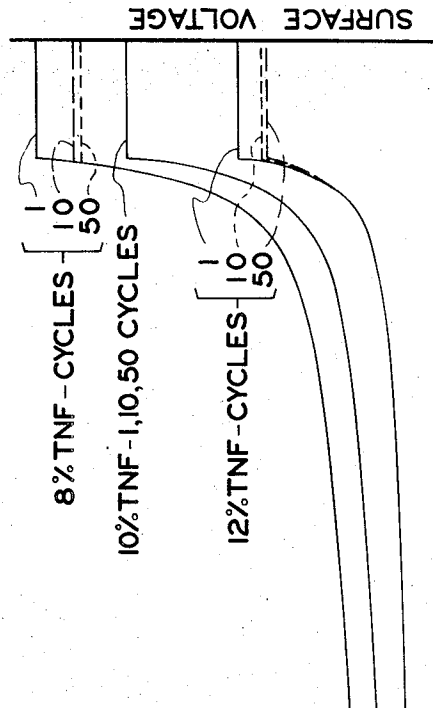


FIG. 5b

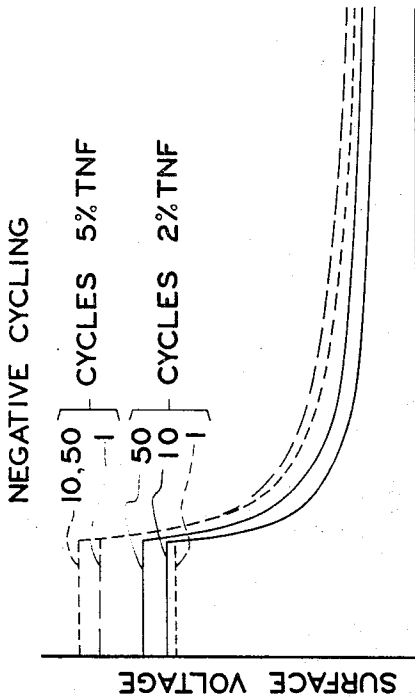


FIG. 4a

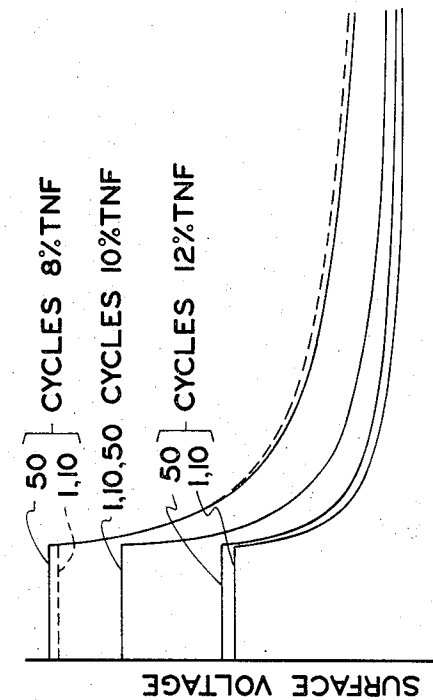


FIG. 5a

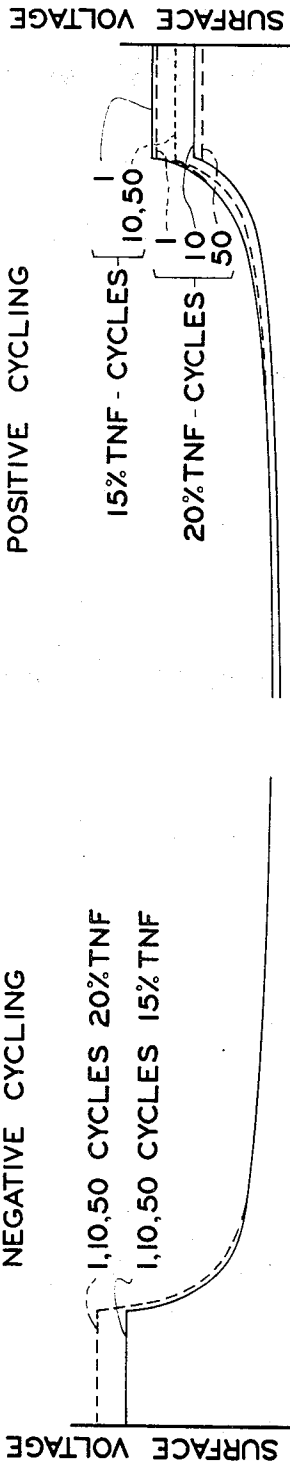


FIG. 6a

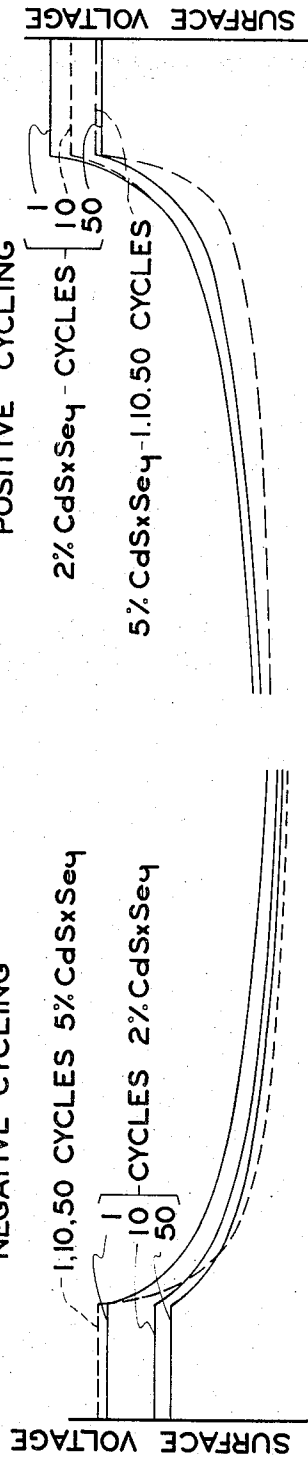


FIG. 9a

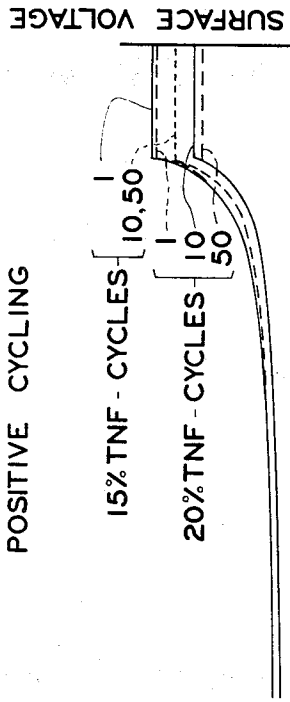


FIG. 6b

FIG. 9b

FIG. 7

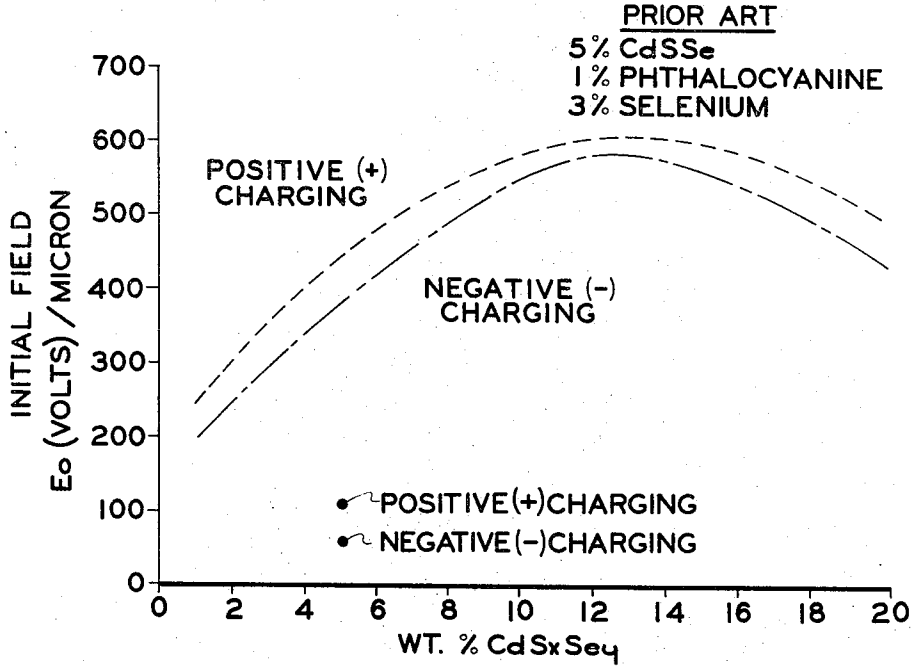
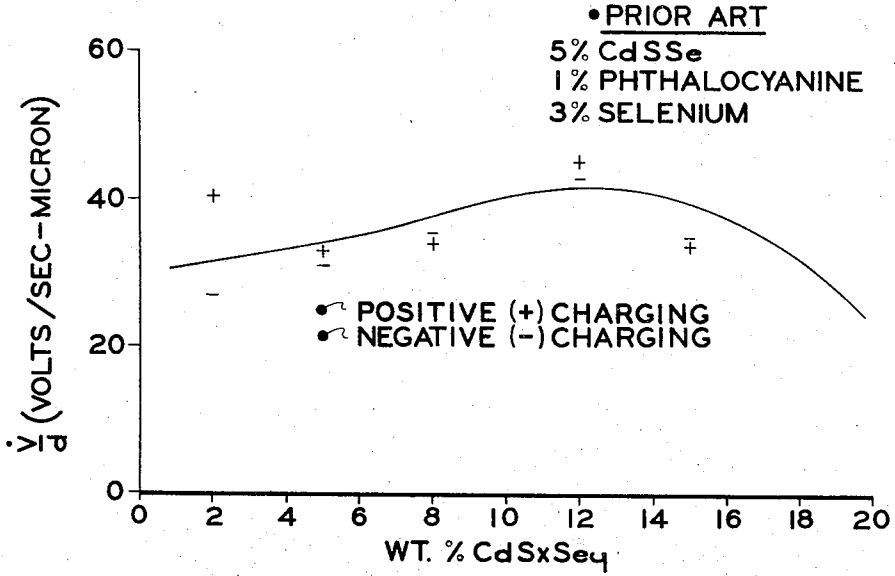


FIG. 8

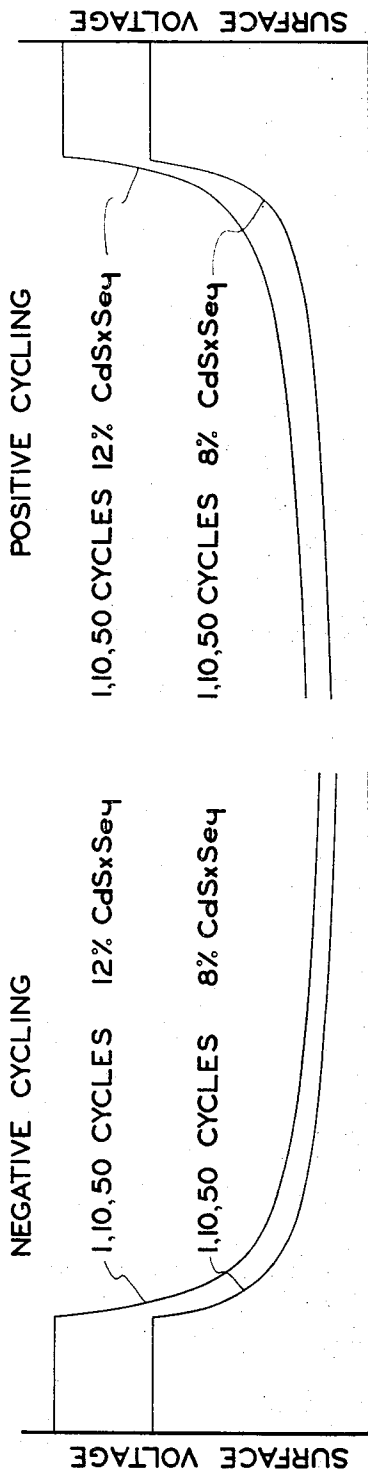


FIG. 10b

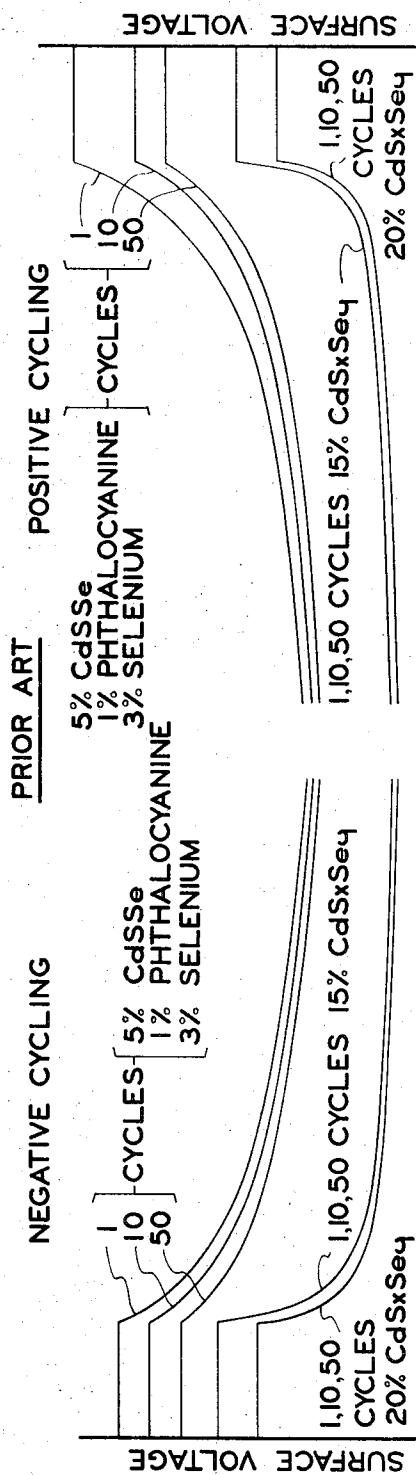


FIG. 10a

FIG. 11b

FIG. 11a

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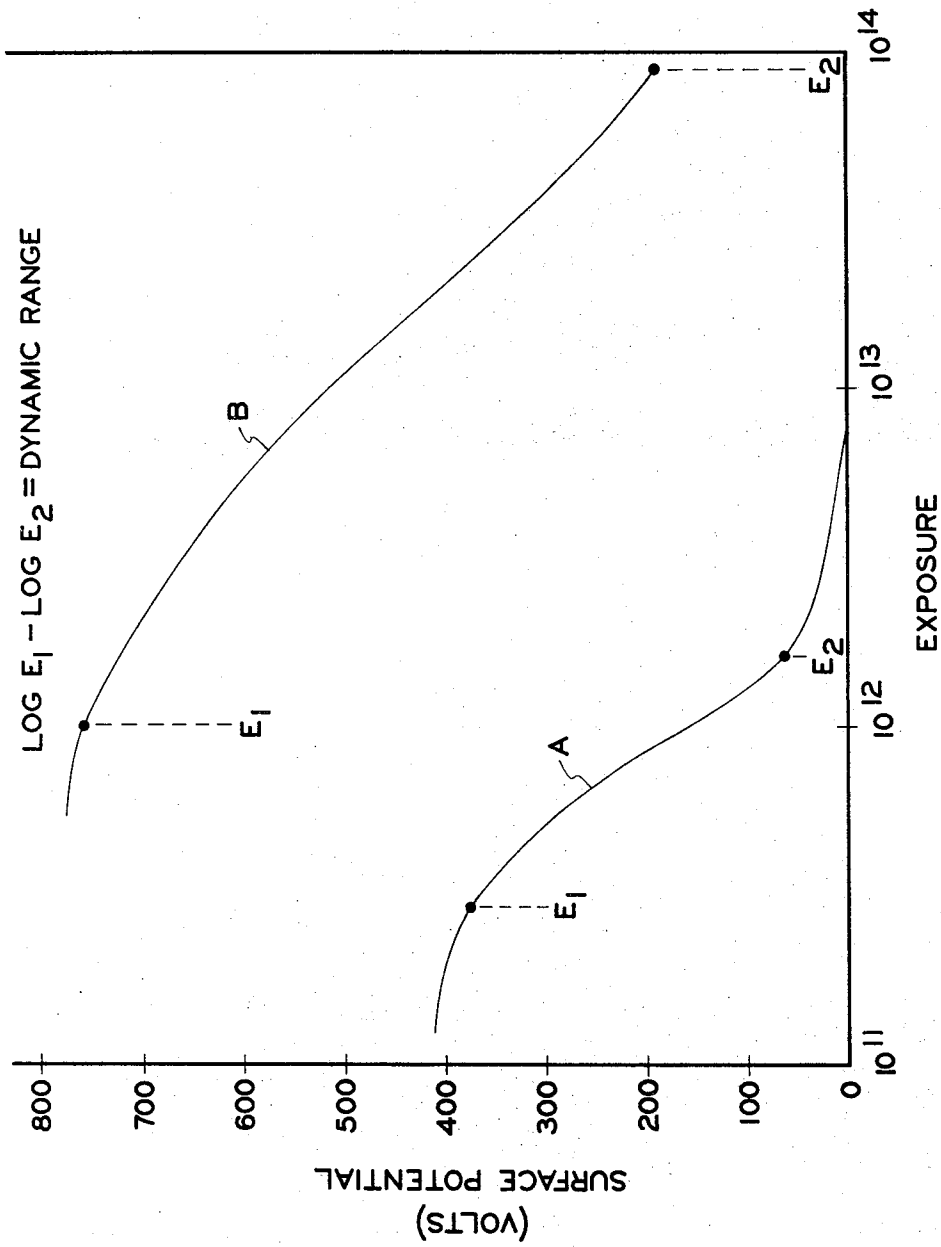


FIG. 12

1

2

3,764,315

AMBIPOLAR ELECTROPHOTOGRAPHIC PLATE
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Filed July 24, 1972, Ser. No. 274,141

Int. Cl. G03g 5/08

U.S. Cl. 96—1.5

16 Claims

ABSTRACT OF THE DISCLOSURE

An ambipolar, electrophotographic plate is disclosed of improved cyclic and discharge characteristics, having a photosensitive binder layer which comprises cadmium sulfoselenide particles, (Cd-S_x-Se_y) dispersed in an ambipolar active matrix binder material in an amount of between about 10 to 15% by weight of said binder. The cadmium sulfoselenide has a stoichiometric relationship of sulfur to selenium, where x is between about 0.1 to 0.6 and y is between about 0.9 to 0.4, to provide a pigment of panchromatic response, and the ambipolar active matrix binder material comprises a mixture of between about 6 to 14% by weight of 2,4,7 trinitro-9-fluorenone in polyvinylcarbazole, to support the injection and transport of photoexcited holes and electrons from the dispersed photosensitive particles through the active matrix binder upon imagewise exposure to radiation without substantial generation of charge carriers itself.

BACKGROUND OF THE INVENTION

This invention relates to an improved ambipolar photoconductive insulating material which, when employed as the photoconductive layer for a xerographic plate and imaged, exhibits superior xerographic characteristics.

In the process of xerography, for example, as described in Carlson Patent 2,297,691, a xerographic plate comprising a layer of photoconductive insulating material on a conductive backing is given a uniform electric charge over its surface and is then exposed to a light and shadow image pattern of the subject matter, the original to be reproduced, usually by conventional projection techniques. This exposure discharges the plate areas in accordance with the radiation intensity that reaches them and thereby creates an electrostatic latent image on or in the photoconductive layer corresponding to the light and shadow image pattern. Development of the latent image is effected by an electrostatically charged, finely divided material such as electrosopic powder, termed "toner" that is brought into surface contact with the photoconductive layer and is held thereon electrostatically in a pattern corresponding to the electrostatic latent image. The developed toner image may be fixed or made permanent on the xerographic plate itself. Alternatively, if it is desired to apply the developed xerographic image to paper, metal, foil, plastic film or other transfer material, the developed image may be transferred from the xerographic plate to such a support surface to which it may be affixed by any suitable means.

Although many photoconductive insulating materials have been disclosed to be useful in the process of xerography, selenium in its amorphous form has heretofore been the preferred material for use in commercial xerographic equipment because of its extremely high quality image capability, relatively high light response, capability to receive and retain charge areas at different potentials, and because of its ability to be employed at high cycling rates for image reproduction.

Although amorphous selenium is by far the most extensively used photoconductive insulating material in com-

mercially available xerographic machines employing reusable xerographic plates, amorphous selenium has certain characteristics which have prompted those skilled in the art to search for alternative materials. For example, amorphous selenium is sensitive only to radiation of wavelengths shorter than about 580 nanometers. In addition, xerographic plates made with amorphous selenium are expensive to manufacture since the selenium itself is expensive and must be applied to the supporting substrate by vacuum evaporation under highly controlled temperature and other conditions, for example, as illustrated in Keck Patent 2,739,079. Also, amorphous selenium layers are only meta-stable because they are recrystallized into inoperative crystallized forms at temperatures only slightly in excess of those prevailing in conventional xerographic copy machines. Also, the surface of an amorphous selenium photoconductor layer is relatively soft and easily abraded which results in deterioration of the plate surface and subsequently, of image quality.

In addition, amorphous selenium photoconductors while producing line copy and other contrasting originals in an excellent fashion, have a relatively short dynamic range of about 0.6 density units when used in combination with conventional xerographic development processes, for example, cascade development. The dynamic range of a particular xerographic plate and development system as used herein is intended to mean that range of original image densities which will produce a viewable change in the density of the reproduction produced by the plate where, density=D=log 1/R where R equals the ratio of reflected light to incident light. For example, in a very dense area of an original or reproduction where only one tenth of the incident light is reflected back to the eye of the viewer, R equals 1/10 and the log of 1/R i.e., density, of course, would be 1. A density of 1.3 is where about 1/20 of the incident light is reflected back to the viewer. Practically, reflection densities anywhere from about 1.2 to 1.5 or above appear to the human eye as a very dense black. Thus, since generally it is thought that a given imaging system should have a dynamic range of about 1.2 or 1.5 or more to produce a quality tone reproduction, with a reasonably full latitude of contrast, it is seen that conventional amorphous selenium plate xerography has serious limitations in this regard.

Also, it has been found that amorphous selenium photoconductors are preferably imaged with positive charge in that such photoconductors have a longer charge transport range for holes and a shorter charge transport range for electrons. Accordingly, as set out herein, the photoconductors of the instant invention may be charged to either polarity, positive or negative, and still be useful in xerography. This desirable characteristic is termed ambipolarity.

Electrically insulating, organic binder, xerographic plates which contain zinc oxide and other pigments, while comparatively inexpensive, are not generally considered to be substantially reusable. Furthermore, it is necessary to use such a high percentage of pigment in order to attain adequate sensitivity that it is difficult in zinc oxide plates to obtain smooth surfaces which would lend themselves to efficient toner transfer and efficient cleaning prior to reuse as required in reusable xerography. For example, in a conventional zinc oxide binder layer, zinc oxide pigment may comprise about one half (about 50%) of the layer by volume, the other half consisting of electrically insulating resin. This relatively high volume of pigment is required to insure that a series of unbroken chains of pigment particles are formed throughout the binder layer thickness to transport the charge carriers. Also, at least as important is that the photoconductive discharge characteristics change with cycling, and the

plates exhibit residual conductivity patterns of previous images, as well as reduced charge acceptance levels. An additional drawback to use of the zinc oxide type plates is that generally they can be sensitized only by negative and not by positive corona, because with this type of plate, the dark conductivity of positive charges is unacceptable.

Thus, although some photoconductive insulators work well in xerography, there is a continuing need for better photoconductive insulating materials for use in fabricating xerographic plates for use in xerography. In particular, it would be extremely desirable to provide an organic binder type xerographic plate which may be sensitized with either polarity of charge, which is reusable, which has a relatively broad spectral response with extended dynamic range and which is relatively easy and inexpensive to manufacture.

In U.S. patent application, Ser. No. 94,072, filed Dec. 1, 1970, a photoconductive member for xerographic applications is disclosed which comprises a mixture of at least two photoconductive pigments capable of generating and injecting holes and electrons dispersed in an active matrix, charge transport binder material, capable of transporting either holes or electrons in response to image-wise radiation. The active matrix binder material disclosed therein comprises very broadly a mixture of about 5 to 15%, preferably about 10%, by weight of 2,4,7 trinitro-9-fluorenone in polyvinyl carbazole, most broadly, the range of addition of the pigment mixture or total pigment content is between about 2 to 10 parts of pigment per 100 parts of binder by volume. In a preferred embodiment, one of the pigments used in the binder layer in addition to selenium and phthalocyanine is cadmium sulfoselenide ($Cd-S_x-Se_y$) in a weight range of $\frac{1}{2}$ to 5 parts per 100 parts of binder material. Plates produced with the above described unique photoconductive materials have superior electrical and imaging characteristics, are operationally capable of handling either positive or negative charging and doing so while exhibiting superior recycling properties and other functional aspects of xerography.

The present invention is an improvement over the above described unique photoconductive material and exhibits improved xerographic characteristics including high speed, recyclability and panchromatic response. The instant invention comprises a photoconductive material utilizing these components within well defined critical limits to yield the above noted improved functional characteristics.

It is therefore an object of this invention to provide a new photoconductive insulating material and processes for making and using the same.

It is a further object of this invention to provide a xerographic plate wherein the photoconductor employs a relatively small, but optimum percentage of a pigment material in an electrically insulating binder.

It is still a further object of this invention to provide a xerographic plate which may be formulated from flexible binder systems suitable, for example, for use in web or endless belt type xerographic plate configurations.

It is still a further object of this invention to provide a pigment insulating binder photoconductor which is ambipolar and which may be used to reproduce positive images from positive or negative originals without changing the developer, magnitude of the coronator voltage, or exposure.

It is still a further object of this invention to provide a pigment insulating binder photoconductor which is recyclable, has superior speed, and exhibits panchromatic response in the process of xerography.

It is also an object of this invention to provide pigment insulating binder photoconductor having an extended dynamic range to permit its use in continuous tone imaging.

It is still a further object of this invention to provide a pigment insulating binder photoconductor which is rela-

tively easy and inexpensive to make, exhibiting no geometrical constraints in fabrication and which has superior mechanical properties.

SUMMARY OF THE INVENTION

In accordance with the present invention, a novel photoconductive material is provided comprising critically defined ranges of components to yield improved functional characteristics for xerography. The components of the novel photoconductive material include an ambipolar active matrix binder material, capable of supporting the injection of holes or electrons and transporting the same under a broad range of operative conditions, consisting of a mixture of between about 6 to 14% by weight, preferably 8 to 12% by weight of 2,4,7 trinitro-9-fluorenone in polyvinylcarbazole, and cadmium sulfoselenide ($Cd-S_x-Se_y$) dispersed uniformly therein in an amount of between about 10 to 15% by weight of said binder, the cadmium sulfoselenide having a stoichiometric relationship of sulfur to selenium wherein x is between about 0.1 to 0.6 and y is between about 0.9 to 0.4.

The above defined critical ranges of components cooperate to yield an ambipolar photoconductive material and plate which is of faster, panchromatic response, and which is recyclable without a significant residual image pattern or sensitivity fatigue. The former effect may also characterize a "ghosting" or retention of a residual latent or "ghost" image which corresponds to prior exposures of the plate and is a particular problem with extensive recycling of a photoconductive material. The instant invention is free from "ghosting" with either polarity of charge and exhibits a wide range of operation, for line or continuous tone imaging.

Xerographic plates made with the improved photoconductive material set forth are easily fabricated because of a minimal number of components, the need for only a single layer of photoconductive material without vacuum evaporation capabilities, and also because the photoconductive layer requires only a relatively low percentage of pigment loading with random distribution thereof, rather than precise or stringent geometric controls of the pigment particle loading. The efficiency of the photoconductive plate which permits a lower loading of photoconductive pigment is of course, related to the ability of the binder material to efficiently effectively transport either holes or electrons without trapping thereof during image-wise exposure, and without significant functionality as an intrinsic photoconductive material because of a relatively small absorption of visible light thus contributing little to photogeneration of carriers.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 depicts the novel photosensitive member of the instant invention and its structure.

FIG. 2 illustrates the photoinduced discharge characteristics or speed of the photosensitive member of the instant invention as a function of the percentages of 2,4,7-trinitro-9-fluorenone in the active matrix binder.

FIG. 3 depicts the initial charge acceptance of the photosensitive member of the instant invention as a function of the percentage of 2,4,7-trinitro-9-fluorenone in the active matrix binder material.

FIGS. 4(a)(b), 5(a)(b) and 6(a)(b) illustrate the cycling properties of the photosensitive member of the instant invention as a function of the percentage of 2,4,7-trinitro-9-fluorenone in the binder material.

FIG. 7 depicts the charge acceptance properties of the photosensitive member of the instant invention as a function of the percentage of cadmium sulfoselenide in the binder material and as compared to similar prior art photosensitive members.

FIG. 8 illustrates the speed or discharge characteristics of the photosensitive member of the instant invention as a function of cadmium sulfoselenide in the binder material

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and as compared to similar prior art photosensitive members.

FIGS. 9(a)(b), 10(a)(b) and 11(a)(b) depict the cycling properties of the photosensitive member of the instant invention as a function of cadmium sulfoselenide in the binder material and as compared to similar prior art photosensitive members.

FIG. 12 graphically illustrates the dynamic range of the photosensitive member of the instant invention as compared to selenium.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to FIG. 1, there is illustrated a xerographic plate 5 comprising a layer of the novel photoconductive material of the instant invention 6 overlying electrically conductive layer 7. In the conventional practice of xerography, the electrically conductive layer 7 is grounded during a charging step to facilitate application of a fairly uniform layer of charge on the layer of material 6. Charging of the plate 5 can be accomplished in a variety of ways, including for example, the rubbing of layer 6 with soft brush or fur or preferably by corona charging techniques, as described in U.S. Patents 2,836,725 and 2,777,957. After charging by a corona charging technique or by the method of choice, the plate is exposed to a pattern of activating radiation in imagewise configuration to selectively discharge the applied charge from areas of the plate struck by the activating radiation, as compared to areas not struck by the activating radiation and thereby form an electrostatic latent image on layer 6.

Thereafter the latent image is then made visible i.e. developed, by contacting the latent image with toner, generally electrostatically charged to a polarity opposite to the polarity of the electrostatic latent image, causing the material to be held thereon in the pattern corresponding to the latent image.

Any suitable development system may be used to develop latent images on plates of this invention and many such systems exist in the art. For example, the system of cascade development has found extensive commercial acceptance and generally consists of gravitationally flowing developer material consisting of two component materials of the type disclosed in Walkup et al. Patent 2,638,416 over the xerographic plate bearing the latent image. The two components consist of toner and a granular material called "carrier" and which by mixing acquire triboelectric charges of opposite polarities. In development, the toner component, usually oppositely charged to the latent image is deposited on the latent electrostatic image to render that image visible.

Typical developing systems include for example, processes shown in Carlson Patents 2,221,776; 2,551,582; 2,690,394; 2,761,416; 2,928,575; Gundlach Patents 3,068,115 and 3,084,043; Mayo Patent 2,895,847; and others.

The powder image may then be transferred to another support surface of which it may be affixed by solvent vapors, heat or other suitable means to render the image permanent or the powder image may be affixed directly to the xerographic plate either as a result of developing or a separate step thereafter.

Layer 7 may be any suitable electrically conductive material, for example, most metals, and the present invention is not limited in this regard. Aluminum has been extensively commercially used in an electrically conductive backing member in the preparation of xerographic plates. However, other suitable materials for this purpose include nickel, steel, brass, metallized tin oxide coated glass, plastics, semi-conductive plastic resins, paper or any other convenient material.

The rigid or flexible plate configuration as shown in FIG. 1 is for illustrative purposes only and the plate configuration may be extensively varied such as the form of a rigid or flexible drum configuration or the form of a

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flexible endless belt in loop of moebius strip form or any other suitable form.

With particular reference to layer 6 and specifically the materials which comprise this layer, the instant invention comprises an improved combination of components set forth within critically defined ranges to yield unexpected and surprising properties. The components including an active matrix binder material capable of transporting both positive and negative charge carriers in response to actinic radiation in imagewise configuration, consisting of a mixture of between about 6 to 14% by weight preferably, 8 to 12% by weight of 2,4,7-trinitro-9-fluorenone in polyvinylcarbazole, and a finely divided cadmium sulfoselenide ($Cd-S_x-Se_y$) photoconductive pigment uniformly dispersed in said active matrix in an amount of between about 10 to 15% by weight, the photoconductive material being capable of generating and injecting holes and electrons into said active matrix binder, and having a stoichiometric relationship of sulfur to selenium wherein x is between about 0.1 and 0.6 and y is between about 0.9 to 0.4.

The use of a binder which is capable of transporting both types of charge carriers results in a highly recyclable plate, at either polarity, thus producing a plate with a broad operational range. The components comprising the ambipolar active matrix binder of the instant invention include a critically defined mixture of between about 6 to 14% preferably 8 to 12% by weight of 2,4,7 trinitro-9-fluorenone which provides electron transport, in polyvinylcarbazole which itself will transport holes. It is this percentage range of 2,4,7 trinitro-9-fluorenone (TNF) which yields an active matrix of optimum ambipolarity without affecting speed or recyclability. Within this initially defined range of TNF, the matrix functions to carry with maximum efficiency either polarity of charge, and without significant charge generation itself when exposed to a wide range of actinic radiation. Furthermore, within this range of TNF concentration the ambipolar matrix cooperates with the recited range of cadmium sulfoselenide ($Cd-S_x-Se_y$) having the prescribed stoichiometric relationship of sulfur to selenium, wherein the composite photoconductor has good recyclability, with improved charge acceptance, and speed for either polarity of charge.

The photosensitive pigment which is dispersed in the ambipolar active matrix material of polyvinylcarbazole and 2,4,7 trinitro-9-fluorenone is a cadmium sulfoselenide pigment ($Cd-S_x-Se_y$) having a particular stoichiometric relationship of sulfur to selenium generally prepared as described in U.S. Pat. 3,151,982. As embodied in the empirical formula, $Cd-S_x-Se_y$, the stoichiometric relation of the sulfur to selenium which is desired in the present invention, is where x is between about 0.1 and 0.6 and y is between about 0.9 to 0.4 and preferably where x is about 0.2 and y is about 0.8. This stoichiometric relationship of sulfur to selenium provides a single photosensitive pigment, which has panchromatic response, thus when employed in an ambipolar active matrix binder material results in a photoconductive material of a wider operative spectral range. Furthermore, this particular stoichiometric relationship of sulfur to selenium also contributes to the speed of the photoconductive material when used in the described ambipolar active matrix binder material, since the described pigment, because of its panchromatic response, utilizes the white light from a constant light source much more effectively than a pigment or mixture of pigments having a narrow spectral range.

The particle size of the $Cd-S_x-Se_y$ pigment as employed in the instant invention is not critical to its practice, although the particle size of the pigment should be less than the overall thickness of the photoconductive binder layer. In general, however, the preferred particle size for the pigment will be about 2 microns or less.

The cadmium sulfoselenide pigment ($Cd-S_x-Se_y$) is added to the recited ambipolar mixture of polyvinylcarbazole

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and 6 to 14% by weight of 2,4,7 trinitro-9-fluorenone, in an amount of between about 10 to 15% by weight of said mixture and uniformly dispersed therein. The described mixture of polyvinylcarbazole and 2,4,7 trinitro-9-fluorenone is capable of efficiently supporting the injection and transport of charges of either polarity from the described photoconductive pigment through the mixture without significant generation of charge carriers itself.

The described percentages of cadmium sulfoselenide ($Cd-S_x-Se_y$), having the recited stoichiometric relationship of sulfur to selenium, is critical to the practice of the instant invention, since the described percentage range of a single pigment in an ambipolar active matrix binder material has been found to yield an improved photoconductive binder material of improved properties including charge acceptance, speed, and cycling properties for either polarity of charge. Furthermore, this percentage range of this particular pigment in the described binder material yields a photoconductive material of improved speed and cyclic properties over a photoconductive member such as in U.S. patent application, Ser. No. 94,072 employing a similar type of active matrix material, but with a mixture of pigments to achieve panchromatic response or with a type of cadmium sulfoselenide pigment being present in an amount of less than 10% by weight of said binder.

This described percentage range of a single pigment further results in a photoconductive material of good mechanical and surficial properties, thus providing a highly functional and smooth photoconductive surface for latent image formation and development, with easy and efficient removal of development material. If the percentage of the described photoconductive pigment is above the recited percentage range, not only are functional characteristics such as speed, and cyclic properties reduced, because of inefficient use of the active matrix binder material as a charge transport medium, but desirable mechanical properties such as stability and adhesion to the substrate are likewise diminished. On the other hand, if the percentage is below the recited range, a photoconductive binder material results of lower speed and cyclic properties than a binder material having the recited percentage of pigment.

The photoconductive binder material of the instant invention additionally yields a photosensitive member, with an extended dynamic range, especially as compared to amorphous selenium. The extended dynamic range of the photosensitive member of the instant invention provides quality tone reproduction with a full latitude of contrast thus making the member eminently suitable for continuous tone imaging.

Referring specifically to FIG. 12, the dynamic range is graphically compared to amorphous selenium. The dynamic range is drawn from the graphical representation by designation of the critical inflection points of the curves (E_1 and E_2) sometimes referred to as the "shoulder" (E_1) and the "toe" (E_2) thereof, then taking the log of this difference as a representation of the dynamic range. In this manner, if curve A for amorphous selenium is examined, it may be seen that the dynamic range is approximately between .6 and .7 units, while if curve B for the photosensitive member of the instant invention is examined, it may be seen that the dynamic range of this member is about 1.5 units. It is therefore apparent from this comparison, that the member of the instant invention has a more dynamic range of operation than amorphous selenium and would be eminently suitable for continuous tone imaging.

It therefore may be seen, that the photoconductive binder material of the instant invention includes a combination of specific materials set forth within critically defined ranges to yield unexpected and surprising properties, including easy formulation in fabrication, relatively low pigment concentration having only random distribution, without stringent geometry controls being imposed, panchromatic response through variations in stoichiometry of the pigment, good speed, acceptable discharge characteristics with either polarity of charge, and improved cycling properties.

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Pursuant to a better understanding of the instant invention, the following examples describing various photoconductive materials of the instant invention, their properties and testing are set forth.

The photoconductive members of the following Examples 1 to 6 which were subjected to the described tests were prepared in each instance as follows:

A 12% solution by weight of polyvinylcarbazole was prepared in a solvent solution comprising on a weight basis, 90% toluene and 10% distilled cyclohexanone. This solution was then shaken for a period of about 6 hours, thus having a viscosity of about 750 centipoises. At this point, the desired weight percentage of 2,4,7 trinitro-9-fluorenone based on weight of PVK was added to the mixture and shaken for a further period of ½ hour.

Following dissolution of the 2,4,7 trinitro-9-fluorenone, the cadmium sulfoselenide pigment ($Cd-S_x-Se_y$) was added to the mixture and shaken for an additional period of about 2 hours. After shaking is completed, the resultant dispersion was stirred to remove any entrapped air bubbles, at which time the solution was ready to be coated on a suitably prepared substrate.

In the instant examples, a flexible substrate such as 6-mil thick ball grained aluminum plate or a 6-mil thick light brush grained, lithographic master plate was employed. In each instance the substrate was first washed with acetone, wiped with lint free paper followed by heating to slightly above ambient temperature to remove residual solvent.

Following preparation of the substrate, a Gardner doctor blade apparatus was used to provide a coating of the photoconductive material on the substrate which was found to vary between 20 to 25 microns in thickness.

After coating, the films were heated at about 100° C. overnight to remove residual traces of solvents.

EXAMPLE 1

A series of seven plates were prepared as described above but with the percentage of 2,4,7 trinitro-9-fluorenone being varied on a weight basis of the polyvinylcarbazole over a range of 2 to 20%, at 2, 5, 8, 10, 12, 15 and 20%. The percentage of cadmium sulfoselenide pigment $Cd_{0.2}Se_{0.8}$ was held constant at 12% by weight of the prepared binder material, with the thickness of the photoconductive layer being generally within the dimensions indicated above.

To evaluate the effect of varying 2,4,7 trinitro-9-fluorenone concentration on the xerographic functionality of the prepared photoreceptors, the photo induced discharge curve of these plates were generally observed and analyzed as described below when the described plates were charged to either a positive or negative polarity.

A single wire, grounded shield corotron charging device was employed with a high voltage power supply generating corona emission of the corotron wire, and all seven of the plates were charged to an approximately uniform surface potential (V_p) at both positive and negative polarities.

Following charging, each plate was exposed to a 1000-watt Xenon arc lamp through the entrance slit of a suitable monochromator having a quartz condensing lens, the light intensity of the system being in the order of 2×10^{14} photons/cm² sec. at 5400 Å. An electronic shutter is further provided to provide a timed exposure mode of operation, and each plate was illuminated for an equal period of time.

Electrical monitoring of the change in potential on the plates is accomplished by the use of a shielded loop probe and an electrometer, the probe shield being referenced to ground in the system and the probe loop monitoring the potential charge as the charged plate is moved under the probe, thus permitting the discharge profile of

each plate to be observed simultaneously with illumination.

The initial change in voltage with respect to time

$$(\dot{v}) \text{ or } \frac{dv}{(dt)}$$

was measured for each plate upon exposure to light and divided by the thickness of the photoconductive layer (d) to normalize the measured changes, making the discharge characteristics proportional to the quantum efficiency of the material. An average reading of these normalized changes in voltage or

$$\frac{\dot{v}}{d}$$

for each polarity of charge are listed below for the varying percentages of 2,4,7 trinitro-9-fluorenone.

Percent TNF	$\frac{\dot{v}}{d}$ (volts/sec./micron)	
	Positive	Negative
2.....	900	660
5.....	790	635
8.....	680	610
10.....	600	580
12.....	520	545
15.....	470	470
20.....	100	285

Referring now to FIG. 2, the above measured data is graphically represented to illustrate the criticality of the percentage of 2,4,7 trinitro-9-fluorenone in the active matrix binder to provide optimum discharge characteristics for either polarity of charge. It may be seen from FIG. 2 that when the percentage of Cd-S_x-Se_y is held constant, and the percent TNF is varied that optimum discharge characteristics result for either polarity of charge when the percentage of TNF in the active matrix binder is between about 6 to 14%, preferably 8 to 12%.

EXAMPLE 2

The seven plates with varying percentages of 2,4,7 trinitro-9-fluorenone as described in Example 1 were then evaluated as to their charge acceptance characteristics to determine the effect of percent TNF on this functional characteristic. The charge acceptance of the plate is broadly defined as the maximum field to which the plate could be charged, expressed as volts/micron. This is an important functional characteristic of electrophotographic plates since the corresponding initial potential, when considered with other factors will determine the maximum degree of contrast that can be achieved during development of the electrostatic images. The seven plates were subjected to a discharge from a corotron operated at a voltage of about 9500 volts at both positive and negative polarities of charge and the charge acceptance measured on an electrometer.

Referring now to FIG. 3, the charge acceptance of plates containing the varying percentages of 2,4,7 trinitro-9-fluorenone are graphically depicted for either polarity of charge, the aim being to determine the optimum amount of charge acceptance equivalent for both positive and negative charging. Again, it may be seen from the depicted graph that optimization of charge acceptance and equivalency for positive and negative charging occurs when the percent TNF is broadly between about 6 to 14%, although superior results occur when the percentage of TNF is between about 8 to 12% by weight, thus further illustrating the ambipolar characteristics of the active matrix binder of the instant invention which are maintained along with superior xerographic functional characteristics, such as charge acceptance.

EXAMPLE 3

To illustrate the optimum percentage of 2,4,7 trinitro-9-fluorenone which is needed in the active matrix binder of the instant invention to provide ambipolarity as well

as desirable and improved cyclic properties, the seven plates described in Example 1 were subjected to a cycling evaluation for both positive and negative charging.

To determine cycling, each plate was exposed to the source of illumination as described in Example 1, and was placed on a moving platen which had a velocity of about 3.5 cm./sec. An elapsed time of about 18 seconds was used, in other words, from the first exposure to light until the second light exposure, a period elapsed of about 18 seconds.

Each plate was cycled 50 times for both polarity of charge and specific changes such as charge acceptance and the photo induced discharge were observed. Referring now specifically to FIGS. 4(a)(b), 5(a)(b) and 6(a)(b), the described measurements are graphically depicted for each percentage of 2,4,7 trinitro-9-fluorenone for each polarity or charge. The y axis of the graph illustrates the surface voltage or potential of the plate and the x axis represents time. The first, tenth and fiftieth cycle are graphically depicted. In those instances where no change in voltage over the measured period of time for up to 50 cycles has taken place, the first, tenth, and fiftieth cycles are superimposed as a single curve.

It may be seen from the depicted cycling tests that optimum stability and sensitivity for cycling also occurs for either polarity of charge when the percentage of 2,4,7 trinitro-9-fluorenone is generally between 8 to 12% by weight of the active matrix binder, and that exceptional stability and sensitivity for both polarities of charge occurs when the percentage of TNF is at about 10%.

EXAMPLE 4

A series of six plates were then prepared in the recited procedure which proceeds Example 1 but with the percentage of 2,4,7 trinitro-9-fluorenone being held constant at 10% by weight of the polyvinylcarbazole to yield an ambipolar active matrix material. The percentage of cadmium sulfoselenide (Cd-S_{0.2}-Se_{0.8}) was however, varied at concentrations of 2, 5, 8, 12, 15 and 20% by weight of the binder material with the thickness of the photoconductive layer for each plate being within the dimensions indicated above and having the respective optical densities listed below in the test data.

An additional plate was also prepared which illustrates the photoconductive member disclosed in U.S. patent application, Ser. No. 94,072, by Bean and Gundlach for comparative testing against the above plates to illustrate the improved xerographic characteristics of the electrophotographic plates of the instant invention. The described prior art plate comprises a mixture of about 10% by weight 2,4,7 trinitro-9-fluorenone in polyvinylcarbazole as the binder material, having dispersed therein as photoconductive pigments about 1% by weight of metal free phthalocyanine, which is prepared as shown in U.S. Pat. No. 3,357,989 to Byrne et al., 3% by weight amorphous selenium, and 5% by weight of cadmium sulfoselenide. The photoconductive binder layer is prepared in a manner similar to that described in the procedure preceding Example 1 and as described in U.S. patent application, Ser. No. 94,072 to Bean and Gundlach and coated on an aluminum substrate.

The above plate, and the preceding six plates were then evaluated as to their charge acceptance in a manner identical to that set forth in Example 2 for both positive and negative polarities of charge.

The results of this testing is graphically illustrated in FIG. 7 in which it may be seen that optimum charge acceptance occurs when the percentage of cadmium sulfoselenide is between about 10 and 15% by weight of said binder and specifically at 12% by weight. Likewise, referring to the prior art plate described above, the charge acceptance is much less at the same percentage of cadmium sulfoselenide and significantly less at the recited range of cadmium sulfoselenide of the instant invention. The improved charge acceptance properties of the plates

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of the instant invention over the prior art materials is therefore appropriately illustrated in FIG. 7.

EXAMPLE 5

The six plates referred to in Example 4 having a varying percentage of cadmium sulfoselenide in addition to the prior art plate described in Example 4, were then evaluated for photodischarge characteristics or speed as set forth in Example 1 for both polarities of charge. The measured initial

$$\frac{dv}{dt} \circ ;$$

normalized for layer thickness is expressed below for each plate along with its appropriate optical absorption.

Percent Cd S _x Se _y	$\frac{b}{d}$ (volts/sec./micron)		Optical absorption (cm. ⁻¹)
	Positive	Negative	
2-----	300	245	5.5×10 ²
5-----	440	385	1.07×10 ³
8-----	540	495	1.55×10 ³
12-----	610	595	2.55×10 ³
15-----	595	580	2.59×10 ³
20-----	495	425	3.98×10 ³
Prior art-----	109	61	-----

Referring now to FIG. 8 in which the above average readings are graphically depicted, it may be seen that optimum speed or discharge results when the percentage of cadmium sulfoselenide is within 10 to 15% by weight of the active matrix binder material for both polarities of charge. Furthermore, as to the prior art plate, it may be seen that a dramatic improvement in speed results even at the same percentage of cadmium sulfoselenide as the prior art plate, and that an even more significant result is achieved when the cadmium sulfoselenide is present in an amount of between about 10 to 15% by weight of said binder.

EXAMPLE 6

The six plates referred to in Example 4 having the varying percentage of cadmium sulfoselenide, as well as the prior art plate also described in Example 4 are then evaluated for their cyclic properties for both polarities of charge in a manner similar to that described in Example 3.

Referring now specifically to FIGS. 9(a)(b), 10(a)(b) and 11(a)(b), the results of the cycling testing is graphically depicted in a manner similar to that which has been previously described in reference to Example 3. It is apparent from the depicted data that the optimum stability and sensitivity when the described plates are used in a cyclic mode, occurs when the percentage of cadmium sulfoselenide is between about 10 to 15%, particularly at 12%. Likewise, with reference to the prior art plate, it may be seen that while the first cycle shows good sensitivity, that as the number of cycles increases, the effect of this repetitive use on sensitivity is illustrated as a reduction in stability of the plate when recycled. It is thus apparent from the above comparative test that even at the same percentage of cadmium sulfoselenide, i.e. 5%, an improvement in recycling properties is seen, with optimum improvement being achieved when the percentage of cadmium sulfoselenide is about 10% or above.

The dramatic improvement of speed, and cyclic properties of the photosensitive member of the instant invention over the prior art is thus illustrated by the above examples, with further illustration being made of the criticality of the recited operative parameters of the novel photoconductive member of the instant invention.

The above examples are merely illustrative of the instant invention and it will be understood that various other changes in the details, materials or steps which

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have been described may be made without departing from the spirit of the instant disclosure, and such changes and other modifications are intended to be included within the scope of the instant disclosure and appended claims.

What is claimed is:

1. An ambipolar electrophotographic plate having a photosensitive binder layer comprising photosensitive particles dispersed in an electronically active organic matrix binder in an amount of from about 10 to 15% by weight of said binder, said photosensitive particles consisting essentially of Cd-S_x-Se_y wherein x is between about 0.1 to 0.6 and y is between about 0.9 to 0.4, said active matrix binder consisting essentially of a mixture of between about 6 to 14% by weight 2,4,7 trinitro-9-fluorenone in polyvinylcarbazole, said active binder being capable of supporting the injection of photo-excited holes and electrons from said photosensitive particles and transporting them through said active matrix material.

2. An ambipolar electrophotographic plate as set forth in claim 1 wherein said active matrix binder consists essentially of a mixture of between about 8 to 12% by weight of 2,4,7 trinitro-9-fluorenone in polyvinylcarbazole.

3. An ambipolar electrophotographic plate as set forth in claim 2 wherein said active matrix binder consists essentially of about 10% by weight of 2,4,7 trinitro-9-fluorenone in polyvinylcarbazole.

4. An ambipolar electrophotographic plate as set forth in claim 1 wherein said photosensitive particles consist essentially of Cd-S_x-Se_y wherein x is about 0.2 and y is about 0.8.

5. An ambipolar electrophotographic plate as set forth in claim 1 wherein said photosensitive particles are present in an amount of about 12% by weight of said active matrix binder material.

6. An ambipolar electrophotographic plate having a photosensitive binder layer comprising photosensitive particles dispersed in an electronically active organic matrix binder in an amount of about 12% by weight of said binder, said photosensitive particles consisting essentially of Cd-S_x-Se_y wherein x is between about 0.1 to 0.6 and y is between about 0.9 and 0.4, said active matrix binder consisting essentially of a mixture of between about 8 to 12% by weight of 2,4,7 trinitro-9-fluorenone in polyvinylcarbazole, said active binder being capable of supporting the injection of photo-excited holes and electrons from said photosensitive particles and transporting them through said active matrix material.

7. An ambipolar electrophotographic plate as set forth in claim 6 wherein said active matrix binder consists essentially of a mixture of about 10% by weight of 2,4,7 trinitro-9-fluorenone in polyvinylcarbazole.

8. An ambipolar electrophotographic plate as set forth in claim 6 wherein said photosensitive particles consist essentially of Cd-S_x-Se_y wherein x is about 0.2 and y is about 0.8.

9. A method of imaging which comprises:

(a) providing a xerographic plate having a photosensitive binder layer comprising photosensitive particles dispersed in an electronically active organic matrix binder in an amount of from about 10 to 15% by weight of said binder, said photosensitive particles consisting essentially of Cd-S_x-Se_y wherein x is between about 0.1 to 0.6 and y is between about 0.9 and 0.4, said active matrix binder consisting essentially of between about 6 to 14% by weight 2,4,7 trinitro-9-fluorenone in polyvinylcarbazole, said active binder being capable of supporting the injection of photo-excited holes and electrons from said photosensitive particles and transporting them through said active matrix material;

(b) uniformly charging said plate, and

(c) exposing said plate to a source of radiation to which the active binder material is substantially transparent whereby injection and transport of photo-generated charges from said photosensitive material

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occurs through said active matrix binder material to form an electrostatic image on said plate.

10. The method of claim 9 which further includes developing said latent image to make it visible.

11. The method of claim 9 wherein said charging step 5 is carried out at a negative polarity.

12. The method of claim 9 wherein said charging step is carried out at a positive polarity.

13. The method of claim 9 wherein said active matrix binder consists essentially of a mixture of between about 8 to 12% by weight of 2,4,7 trinitro-9-fluorenone in 10 polyvinylcarbazole.

14. The method of claim 13 wherein said active matrix binder consists essentially of a mixture of about 10% by weight of 2,4,7 trinitro-9-fluorenone in polyvinylcarbazole. 15

15. The method of claim 9 wherein said photosensitive particles are present in an amount of about 12% by weight of said active matrix binder material.

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16. The method of claim 9 wherein said photosensitive particles consist essentially of $Cd-S_x-Se_y$ wherein x is 0.2 and y is 0.8.

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U.S. Cl. X.R.

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