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[56] **References Cited**

UNITED STATES PATENTS			
2,803,542	8/1957	Ullrich	96/1
2,956,023	10/1960	Fredrick et al.	252/62.3
3,172,828	3/1965	Shepard et al.	204/18
3,252,874	5/1966	Hamm et al.	204/18
3,312,548	4/1967	Straughan	96/1.5
3,427,157	2/1969	Cerlon	96/1.4

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[54] **INDIUM DOPING OF SELENIUM-ARSENIC PHOTOCONDUCTIVE ALLOYS**
16 Claims, 2 Drawing Figs.

[52] U.S. Cl. **96/1.5,**
96/1, 252/501, 252/62.3, 75/134

[51] Int. Cl. **G03g 13/22,**
G03g 5/02

[50] Field of Search **252/501,**
62.3; 96/1.5; 75/134

ABSTRACT: A xerographic plate having a novel photoconductive layer comprising a vitreous selenium-arsenic alloy containing indium in an amount sufficient to enhance the electrical characteristics of the plate.





FIG. 1

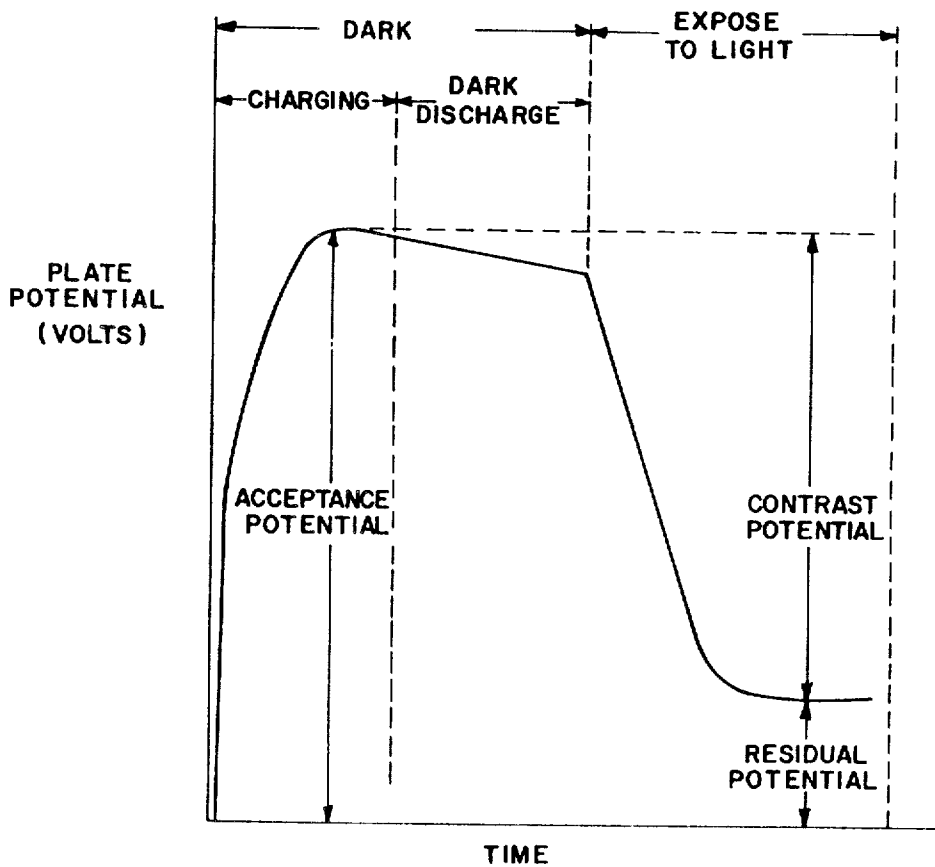


FIG. 2

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INDIUM DOPING OF SELENIUM-ARSENIC PHOTOCONDUCTIVE ALLOYS

BACKGROUND OF THE INVENTION

This application relates to xerography, and more specifically to a novel photoconductive composition.

In the art of xerography, a xerographic plate containing a photoconductive insulating layer is imaged by first uniformly electrostatically charging its surface. The plate is then exposed to a pattern of activating electromagnetic radiation such as light, which selectively dissipates the charge in the illuminated areas of the photoconductive insulator while leaving behind a latent electrostatic image in a nonilluminated area. This latent electrostatic image may then be developed to form a visible image by depositing finely divided electroscopic marking particles on the surface of the photoconductive insulating layer. The concept of xerography was originally described by Carlson in U.S. Pat. No. 2,297,691, and is further amplified and described by many related patents in the field.

The discovery of the photoconductive insulating properties of highly purified vitreous selenium has resulted in this material becoming a standard in commercial reuseable xerography. U.S. Pat. No. 2,970,906 to Bixby, describes the use of vitreous selenium in xerography. An outstanding characteristic of vitreous selenium is its capability of holding and retaining an electrostatic charge for relatively long periods of time when not exposed to light, and the fact that it is relatively sensitive to light when compared to many other photoconductive materials. In addition, vitreous selenium has sufficient strength and stability to be reused thousands of times.

The addition of arsenic to selenium has been found to significantly reduce the susceptibility of selenium to diliterious crystal growth during use. U.S. Pat. Nos. 2,803,542 to Ullrich and 2,822,300 to Mayer et al. both disclose improving the properties of vitreous selenium by the incorporation of elemental arsenic in amounts from about 0.1 to 50% by weight. In addition to increasing the resistance to crystallization by the use of arsenic; halogens such as iodine and chlorine, have also been added to selenium-arsenic alloys in order to improve their electrical characteristics such as sensitivity and spectral response. This concept is set forth in U.S. Pat. No. 3,312,548 to Straughan.

In imaging xerographic plates using alloys of the selenium-arsenic system, such as those described above, it is important in the developing cycle that the xerographic plate which contains the latent electrostatic image contain a sufficient potential in the image areas (i.e. those areas in which the toner particles are to be attracted) in order that quality copies having high resolution and density are maintained with consistency. The potential used to describe that which is available for developing a latent electrostatic image is called the contrast potential and may be defined as the difference between the apparent voltage on the surface of a xerographic plate and the level of residual voltage of the plate. Residual voltage or potential may be defined as the apparent surface voltage remaining in light exposed areas of the photoconductive surface. High levels of residual potential are a particular problem in reuseable xerography in that a photoconductive plate which is cycled thousands of times inherently builds up a certain amount of residual potential due to the thousands of exposure to light which occur during the xerographic cycling. The relationship between residual potential and contrast potential can be illustrated by a simple example. If in one case a xerographic plate is charged to a retained surface potential of 300 volts and exhibits a theoretical perfect discharge, it will have zero residual potential. Thus, the effective voltage or contrast potential available for development if 300 volts (assuming no dark discharge). If, on the other hand, another xerographic plate is charged initially to a retained potential of 300 volts, but has a residual potential of 200 volts, it can be seen that the difference between the residual and initial voltage is only 100 volts. This 100 volts is the effective voltage available for development (i.e. the contrast potential) of the latent electro-

static image. It can be clearly seen that it is of great significance in imaging xerographic plates in reuseable xerography that the residual voltage be kept at the lowest possible minimum in order that a given xerographic plate may have a maximum contrast potential.

OBJECTS OF THE INVENTION

It is, therefore, an object of this invention to provide a photoconductive composition which exhibits a low residual potential.

It is a further object of this invention to provide an imaging system utilizing a novel photoconductive composition having improved electrical characteristics.

It is another object of this invention to provide an improved xerographic plate utilizing alloys of the selenium-arsenic system which include a small amount of indium.

BRIEF DESCRIPTION OF THE INVENTION

The foregoing objects and others are accomplished in accordance with this invention by providing a xerographic plate which includes a novel vitreous selenium-arsenic alloy which contains a small but critical amount of indium. It has been discovered that the addition of indium to selenium-arsenic alloys yields particularly outstanding results with regard to lowering residual potential and thus increasing the contrast potential available for xerographic development. It should be further noted that other electrical properties such as dark discharge and spectral sensitivity are in no way adversely affected by indium doping, and in fact in some cases even show enhanced spectral sensitivities. The advantages of this improved photoreceptor will become apparent upon consideration of the following disclosure of the invention; especially when taken in conjunction with the accompanying drawings wherein:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic sectional view of one form of a xerographic plate according to the invention.

FIG. 2 illustrates a characteristic charging and discharge curve for one embodiment of a xerographic plate falling within the scope of the instant invention.

FIG. 1 illustrates one embodiment of an improved xerographic plate 10 according to the invention. Reference character 11 designates a support member which is preferably an electrically conductive member. This is conventionally a metal plate such as brass, aluminum, gold, platinum, steel or the like. The support member may be of any convenient thickness; rigid, flexible, in the form of a sheet, a web, a cylinder or the like, and may be coated with a thin layer of plastic. It may also comprise such other materials such as metallized paper, plastic sheets covered with a thin coating of aluminum or copper iodide, or glass coated with a thin conductive layer of chromium or tin oxide. An important consideration is that the member be somewhat electrically conductive or have a conductive surface or coating and that it be strong enough to permit a certain amount of handling. In some instances the support 11 may even be dispensed with entirely. Reference character 12 designates a photoconductive insulating layer which is coated on member 11. The novel composition of layer 12 comprises a vitreous selenium-arsenic alloy containing arsenic in an amount ranging from about 1 to 50% by weight, and a sufficient amount of indium in order to enhance its electrical characteristics. Arsenic in the range of about 0.1 to 20% is preferred in that low arsenic concentrations, when doped with indium show the best electrical properties. Optimum results occur with arsenic in a more preferred concentration of about 0.1 to 0.5%. The indium should be present in an amount ranging from about 1 to 2000 parts per million. A range of indium of from about 1 to 200 parts per million is preferred with about 15 to 50 parts per million yielding particular preferred results.

The thickness of photoconductive layer 12 is not particularly critical in that it may be used in any convenient thickness depending upon its xerographic application. For example, for general commercial applications of a photoconductive layer for xerography, the thickness will generally be about 20 to 80 microns. Thicknesses, however, up to about 300 microns may also be used, and those below 20 microns are also included within the scope of this invention.

Plates containing the novel photoconductive composition of the instant invention may be prepared by any suitable technique. For example, the appropriate proportion of arsenic and selenium may be mixed together and the desired amount of indium added to the mixture. This mixture may then be heated above its melting point and applied in a molten condition to a conductive backing. A particularly satisfactory technique involves vacuum evaporation in which a prealloy or master alloy comprising the desired proportions of arsenic, selenium and indium is first prepared. This master alloy is then placed in an inert crucible contained within a vacuum chamber and heated to evaporate a thin vitreous film of the selenium-arsenic, indium doped alloy onto a supporting substrate usually suspended above the evaporation crucible. In this technique, the vacuum conditions typically may vary from about 10^{14} to 10^{17} Torr. Another typical method of evaporation includes flash evaporation under vacuum conditions similar to those defined above in which a powder comprising an alloy mixture of the desired proportions is selectively dropped into a heated crucible maintained at an elevated temperature. The vapor formed is evaporated upward onto a substrate supported above the crucible. In both of the above methods of vacuum evaporation, the substrate onto which the photoconductive material is condense is usually maintained at a temperature in the range of about 50° to 80° C. for low arsenic concentrations. When the alloy contains arsenic in amounts approaching 40% arsenic the substrate temperature may be as high as 180° to 200° C. If desired, a water cooled platen or other suitable cooling means may be used in order to maintain a constant substrate temperature.

The crucibles which are used for evaporation of the photo-receptor layers of the given invention may be of any inert material such as quartz, molybdenum, stainless steel, etc. U.S. Pat. Nos. 2,803,542 to Ullrich; 2,822,300 to Mayer et al.; 2,901,348 to Dessauer et al.; 2,963,376 to Schaffert; and 2,970,906 to Bixby all illustrate typical vacuum evaporation techniques which are suitable for forming photoconductive layers of the instant invention.

FIG. 2 illustrates a typical charging and discharge curve for a xerographic plate falling within the scope of the instant invention. As shown in the figure, the potential of the plate is shown at various stages or times during the xerographic cycle. The plate is initially charged in the dark to a given potential called the "acceptance potential." After the plate has been charged, a relatively small voltage loss called "dark discharge" occurs. When the plate is imaged by exposure to light, a rapid discharge of the plate occurs in the exposed areas as shown by a near vertical line of the discharge curve. Most of the voltage in the light struck areas is lost due to conduction of holes or electrons through the photoconductive layer which becomes electrically conductive during exposure to light. The plate does not normally discharge down to zero potential, but levels out at a potential called the "residual potential," a level below which a given plate cannot normally be discharged. As previously defined, residual potential is the apparent surface voltage remaining in the light exposed area of the photoconductive surface. It is desirable to obtain as low a residual potential voltage (i.e. that is approaching zero) as possible. With regard to xerographic development, the amount of voltage available for development may be referred to as the "contrast potential," and is defined as that voltage different between that remaining on the plate prior to exposure to light and the residual potential.

As previously stated, it has been discovered that the addition of indium in small but critical amounts to selenium-arsenic alloys has the effect of lowering the residual potential

and hence increase the contrast potential available for development of xerographic images.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples further specifically define the present invention with respect to a method of making and testing a selenium-arsenic photoreceptor containing a small but critical amount of indium. The percentages in the disclosure, examples, and claims are by weight unless otherwise indicated. The following examples and data are intended to illustrate various preferred embodiments of the instant invention.

EXAMPLE I

A mixture of a selenium-arsenic alloy containing one-half percent arsenic and the balance selenium in the form of pellets ranging in diameter from about one-eighth to three-sixteenth inches is physically mixed with indium in a concentration of about 30 parts per million. This mixture is placed in a Pyrex ampul which is evacuated and sealed. The ampul containing the alloy mixture is then placed in a muffle furnace and reacted at a temperature of about 260° C. for 24 hours while being rocked in a device contained within the furnace to insure a homogeneous alloy mixture. After 24 hours the ampul containing the alloy mixture is removed from the furnace and immediately quenched in liquid nitrogen. A vitreous selenium arsenic alloy doped with 30 parts per million indium is removed from the glass ampul and broken up and crushed into relatively small pieces which are suitable for vacuum evaporation.

EXAMPLE II

A xerographic drum having a vitreous layer of a selenium-arsenic alloy containing one-half percent arsenic doped with 30 parts per million indium is formed in the following manner: A hollow aluminum cylinder 4% inches in diameter and 10% inches long is supported for rotation about 12 inches above an SiO coated stainless steel crucible containing a sample of the indium doped selenium-arsenic alloy formed by example I. The crucible and drum are contained within a vacuum evaporation chamber and the chamber evacuated to the vacuum of about 5×10^{15} Torr. The boat containing the indium doped selenium-arsenic alloy is then heated by raising the boat to a temperature of about 350° C. while the surface of the aluminum drum is maintained at a temperature of about 60° C. The boat temperature is maintained for a period of about 1 hour while the aluminum substrate is rotated at about 10 to 15 revolutions per minute forming a vitreous alloy coating on the drum surface. Following the vacuum evaporation, the chamber is then cooled to room temperature, the vacuum broken, and the alloy coated drum removed from the chamber.

A series of 11 aluminum drums containing selenium alloyed with one-half percent arsenic and doped with varying amounts of indium were prepared by the techniques set forth in examples I and II. These drums are then tested to measure residual voltage and contrast potential. The results of these tests are summarized in the table below.

TABLE

Drum No. (Se+1/2As)	% Indium (p.p.m.)	C.P. (Contrast Potential)	V _e (Residual Voltage)
1	1	710	20
2	10	720	40
3	15	580	5
4	30	690	0
5	30	750	10
6	50	680	0
7	50	690	20
8	100	720	50
9	100	710	40
10	200	675	15
11	200	675	15

The values set forth in the table above are obtained by the following test procedure:

1. The photoconductive surface of the drum is charged with a corona charging device to a uniform surface potential of about 800 volts positive potential. The charge on the surface of the drum is then erased by exposure to a white erase lamp to remove the electrostatic charge on the surface of the drum. The charging and erase cycle is repeated 50 times. This cycling or break-in technique simulates the fatigue effect of light on the surface of the photoconductive layer in cyclic operation.

2. Following the 50 cycles, the drum is then charged to a retained surface potential of 800 volts. The corotron charging device is turned off the surface of the drum uniformly exposed to the white erase lamp. The potential on the drum surface after exposure to white light is then measured as the residual potential still remaining on the surface of the plate after exposure to light.

3. The drum is then recharged to a positive potential of 800 volts. The difference between the 800 volts and the residual potential, measured in (2) above, is the contrast potential or actual voltage available for development of a latent electrostatic image.

The dark discharge may be determined by maintaining the drum in the dark and measuring the voltage on the surface of the plate after 30 seconds, and then after 3 minutes. The ratio of the amount of voltage lost to the initial charge potential of 800 volts can then be expressed as a percentage of dark discharge at both 30 seconds and at 3 minutes.

It can be seen from the test results of the table that the indium doped selenium-arsenic alloy exhibits extremely low residual voltages, and hence correspondingly high contrast potentials for concentrations of about 1 to 200 parts per million indium, and particularly outstanding results in the range of about 15 to 50 parts per million. An examination of the data shows the residual voltage averages somewhere between 5 to 50 volts. It should be noted that the improvements shown by indium doping selenium-arsenic alloys of the instant invention reduce the residual voltage to a lower level than exhibited by undoped selenium-arsenic alloys. For example, typical values for residual voltages for undoped selenium-arsenic alloys containing one-half percent arsenic are in the vicinity of 100 volts, while the average residual voltage for indium doped alloys of the same composition is in some instances down to zero, with the average residual voltage being well under 50 volts.

In addition to the advantages, set forth above, the photosensitive composition of the instant invention exhibits excellent speed and spectral response characteristic of the selenium-arsenic alloys set forth in the Ullrich, Mayer et al. and Straughan patents referred to above.

Although specific components and proportions have been stated in the above description of the preferred embodiment of this invention, other suitable materials and procedures such as those listed above may be used with similar results. In addition, other materials and modifications may be utilized which

synergize, enhance, or otherwise modify the photoreceptor layer.

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

What is claimed is:

1. A photosensitive composition comprising a vitreous alloy of selenium, arsenic and indium, with the indium being present in an amount from about 1 to 2000 parts per million.

2. The composition of claim 1 in which the arsenic is present in an amount up to about 20%.

3. The composition of claim 1 in which the indium is present in an amount from about 1 to 200 parts per million.

4. The composition of claim 1 in which the indium is present in an amount of from about 15 to 50 parts per million.

5. A xerographic plate including a photoconductive layer comprising a composition of selenium, arsenic, and indium, the arsenic being present in an amount up to about 50%, with the indium being present in a concentration of about 1 to 2000 parts per million.

6. The plate of claim 5 in which the arsenic is present in an amount up to about 20% and the concentration of indium is from about 1 to 200 parts per million.

7. The plate of claim 5 in which the arsenic is present in an amount from about 0.1 to 0.5%.

8. The plate of claim 7 in which the indium is present in an amount of from about 1 to 200 parts per million.

9. The plate of claim 8 in which the indium is present in an amount of about 15 to 50 parts per million.

10. A photosensitive element comprising:

a. a supporting substrate,

b. an insulating photoconductive composition overlaying said substrate comprising a vitreous selenium-arsenic alloy containing indium in an amount from about 1 to 2000 parts per million.

11. The element of claim 10 in which the arsenic is present in an amount up to about 20%.

12. The plate of claim 11 in which the indium concentration is about 1 to 200 parts per million.

13. A method of imaging comprising:

a. providing a xerographic plate which includes a photoconductive layer of an indium doped vitreous selenium-arsenic alloy containing indium in a concentration of about 1 to 2000 parts per million,

b. forming a latent electrostatic image on the surface of said plate, and

c. developing said image to make it visible.

14. The method of claim 13 in which the indium concentration is about 1 to 200 parts per million.

15. The method of claim 13 in which the arsenic is present in an amount up to about 20%, and the indium concentration is from about 1 to 200 parts per million.

16. The method of claim 13 in which the arsenic is present in an amount of from about 0.1 to 0.5%.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,615,413 Dated October 26, 1971

Inventor(s) Carl B. Fisher et al

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

IN THE SPECIFICATION:

Column 1, line 62, "exposure" should read
--exposures--.

Column 1, line 69, "if" should read --is--.

Column 3, line 24, " 10^{14} to 10^{17} " should
read -- 10^{-4} to 10^{-7} --.

Column 4, line 44, " 5×10^{15} " should read
-- 5×10^{-5} --.

IN THE CLAIMS

Column 6, Claim 6, line 3, "abut" should read --about--.

Column 6, Claim 8, line 2, "abut" should read -- about --.

Signed and sealed this 2nd day of May 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents