Sept. 16, 1969 V. E. STRAUGHAN 3,467,548
METHOD OF MAKING XEROGRAPHIC PLATE BY VACUUM EVAPORATION OF SELENIUM ALLOY
Original Filed Dec. 27, 1965 2 Sheets-Sheet 1



FIG. 1



FIG. 2

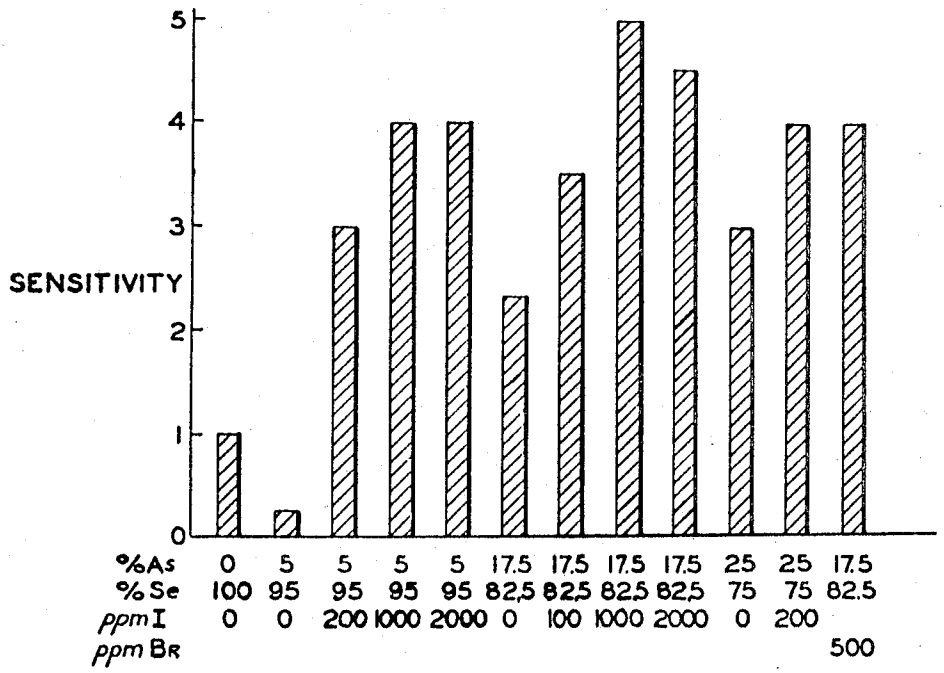


FIG. 3

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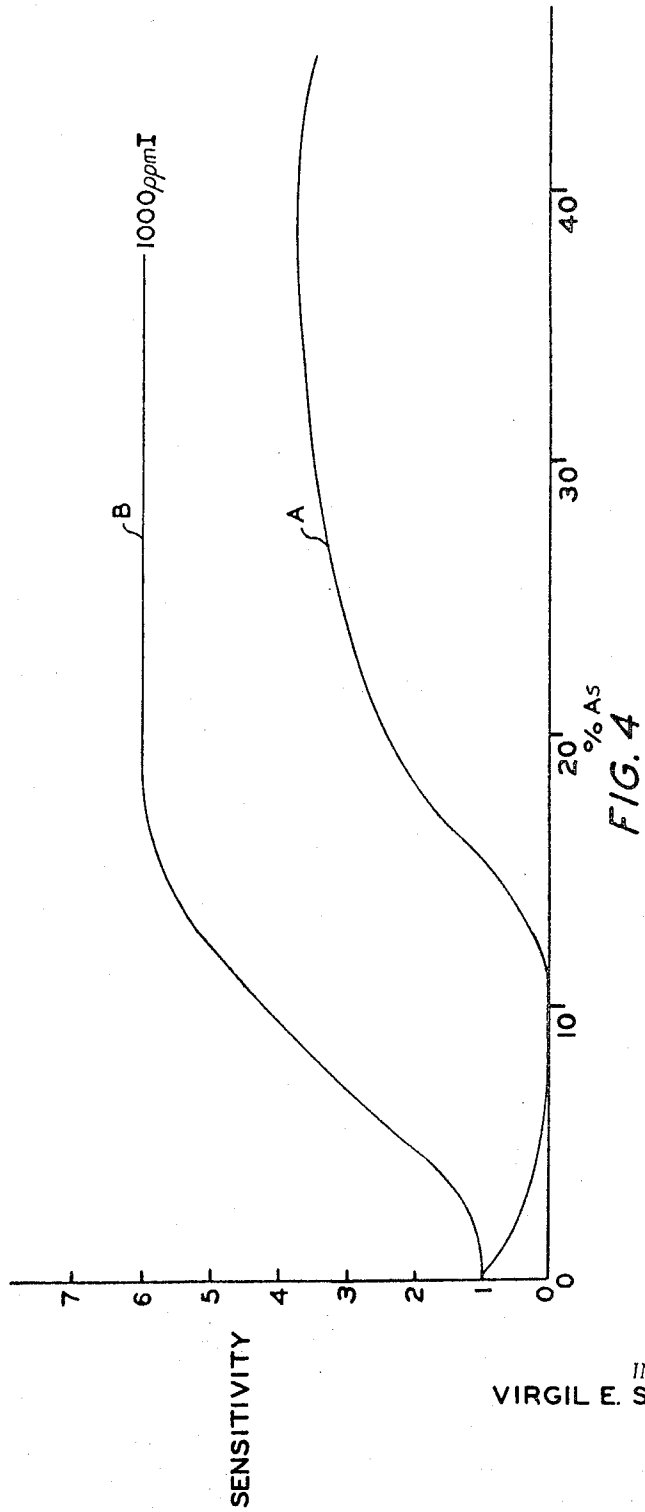


FIG. 4

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METHOD OF MAKING XEROGRAPHIC PLATE BY VACUUM EVAPORATION OF SELENIUM ALLOY

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Application Dec. 27, 1965, Ser. No. 516,529, now Patent No. 3,312,548, which is a continuation-in-part of application Ser. No. 293,357, July 8, 1963. Divided and this application May 31, 1966, Ser. No. 571,150

Int. Cl. H01b *1/02*; B44d *1/18*; C23c *13/02*

U.S. Cl. 117—217 4 Claims

ABSTRACT OF THE DISCLOSURE

A method of making a xerographic plate which comprises vacuum evaporating a mixture of selenium, arsenic, and halogen onto an electrically conductive support member to form a photoconductive alloy layer thereon. The mixture comprises arsenic in a range of about 0.5 to 50 percent by weight, a halogen in range of about 10 to 10,000 part per million, with a balance of the mixture comprising selenium.

This application is a divisional application of applicant's parent application Ser. No. 516,529 filed on Dec. 27, 1965, and now U.S. Patent No. 3,312,548, which in turn is a continuation-in-part of applicant's copending application Ser. No. 293,357 filed July 8, 1963, and now abandoned.

This invention relates to xerography and more specifically to a system utilizing an improved photosensitive plate.

In the art of xerography, it is usual to form an electrostatic latent image on a member or plate which comprises a substantially electrically conductive backing member such as for example, a paper or a metallic member, having a photoconductive insulating surface thereon. It has previously been found that a suitable plate for this purpose is a metallic member having a layer of vitreous selenium. Such a plate is characterized by being capable of receiving a satisfactory electrostatic charge and selectively dissipating such charge when exposed to a light pattern and, in general, is largely sensitive to light in the blue and blue-green spectral range.

In the usual form of xerography, the electrostatic charge pattern formed by the selective dissipation of charge noted above is converted into a visible image through the selective attraction of marking particles by known methods of image development. The xerographic plate is accordingly of great importance in the xerographic process as it is the element responsible for the creation of the charge pattern. Other forms of xerographic plates are known including, for example, sheets of paper coated with a photoconductive mixture of zinc oxide particles in an insulating resin. However, the vitreous selenium xerographic plate remains the most

widely used because it is capable of holding an electrostatic charge for long periods of time when not exposed to light, because it is relatively sensitive to light compared with other xerographic plates, and because it has sufficient strength and stability to be reused hundreds or even thousands of times. The selenium plate, however, is susceptible to deleterious crystal growth when the plate is heated during operation. This growth of crystals in the selenium layer destroys the photoconductive insulating properties of the selenium, and places a limit upon the effective life of the selenium plate.

At the same time, improvements in the light sensitivity and response to longer wavelengths are much desired. A significant contribution was made by O. S. Ullrich in the U.S. Patent 2,803,542, which disclosed that the addition of arsenic to selenium causes a general increase in the light sensitivity of the xerographic plate and also causes the plate to be sensitive to longer wavelengths of light.

There is still, however, a continuing need for plates which require still shorter exposure times and yield a wider range of reproducible colors.

It is, therefore, an object of this invention to provide an improved selenium-arsenic xerographic plate and an improved method for preparing a selenium-arsenic xerographic plate which overcomes the above noted disadvantages.

It is another object of this invention to provide a selenium-arsenic xerographic plate having increased light sensitivity.

It is a further object of this invention to provide a selenium-arsenic xerographic plate having a broadened range of spectral response.

It is yet a further object of this invention to provide an improved method of making selenium-arsenic xerographic plates having increased light sensitivity and a broadened range of spectral response.

It is another object of this invention to provide a selenium-arsenic xerographic plate having improved thermal stability.

The foregoing objects and others are accomplished in accordance with this invention by preparing a xerographic plate containing selenium, arsenic, and up to 10,000 parts per million (p.p.m.) of at least one member of the halogen family. In the preparation of this plate suitable quantities of selenium, arsenic, and a halogen are sealed in a container and reacted at an elevated temperature to form homogeneous mixture of these elements. The alloy is then cooled and applied to a suitable conductive supporting base by vacuum evaporation. When the evaporation process is completed, a finished plate is removed from the vacuum chamber.

In general, the effective range of arsenic in the selenium layer is about 0.5 to 50 percent by weight with the preferred range being about 1 to 25 percent. The lower limit of about 1 percent is dictated by the fact that arsenic in amounts as low as 0.5 percent raises the crystallization temperature and 1 percent practically eliminates crystallization. The upper limit of 25 percent is chosen because this amount of arsenic in combination with halogen doping will achieve essentially the same de-

gree of light sensitivity and broadened spectral response as As_2Se_3 or 38.5 percent arsenic, without introducing the high dark discharge property of As_2Se_3. The upper end of the preferred range, from 15 to 20 percent arsenic, would be more desirable from the standpoint of obtaining the optimum light sensitivity.

The effective range of the halogen addition is from about 10 to 10,000 parts per million with about 100 to 5,000 parts per million being preferred. The sensitivity for a given amount of arsenic increases to a certain degree with increased amounts of the halogen. Although amounts of 10 parts per million do exhibit an increased sensitivity a more desirable sensitivity value can be obtained with greater amounts, such as at least 100 parts of the halogen. Similarly amounts as high as 10,000 parts per million (1 percent) are effective, but are unnecessary in most cases, in that there is no significant change over the use of 5000 parts per million.

The selenium-arsenic-halogen composition may comprise the entire insulation layer or be present as a thin outer layer overlaying a base layer of pure selenium.

The advantages of the improved xerographic plate and the method for producing said plate will become more apparent upon consideration of the following disclosure of the invention; especially when taken in conjunction with the accompanying drawings wherein:

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

FIG. 2 is a schematic sectional view of a second form of xerographic plate according to the invention;

FIG. 3 is a bar graph showing the relative sensitivity of various xerographic plates;

FIG. 4 shows the relative sensitivity of a selenium plate with increasing amounts of arsenic, with and without the addition of a halogen.

The halogen is primarily illustrated by the use of iodine in FIGURES 1 to 4.

FIGURE 1 shows a first form of improved xerographic plate according to the invention. Reference character **10** designates an electrically conductive mechanical support 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 or 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 as metallized paper, plastic sheets covered with a thin coating of aluminum or copper iodide, or glass coated with a thin layer of chrominum or tin oxide. An important consideration is that the member be at least somewhat electrically conductive or have a somewhat conductive surface and that it be strong enough to permit a certain amount of handling. Member **11** may even be dispensed with entirely in some cases. Reference character **12** designates the photoconductive insulating layer which is coated on member **11**. As shown in the figure, this layer is comprised of vitreous selenium together with lesser amounts of arsenic and a halogen consisting of iodine, bromine, chlorine or fluorine. As shown in the xerographic art, this layer may be as thin as about 1 micron or as thick as about 300 microns or more, but for most commercial applications the thickness will generally lie between about 20 to 80 microns. This range of 20 to 80 is preferred in that the thicker layers (i.e. those approaching 300 microns) show some signs less desirable adherence to the support member than lesser thickness. A suitable method of making the plate of FIGURE 1 is described below for illustrative purposes only.

Suitable quantities of selenium, arsenic, and iodine are sealed in a reaction vessel and reacted at 525° C. for three or four hours in a rocking furnace. After the selenium mixture is cooled and removed from the reaction vessel, it is applied to a suitable support member **10**, such as a sheet of polished brass, by a vacuum evaporation process. The mixture is placed in a crucible within a bell jar and the brass plate is supported about 12 inches above the crucible and maintained at a temperature of about 70° C. The bell jar is evacuated to a pressure of about 5×10^{-5} torr and the crucible is heated to evaporate the selenium mixture onto the support member **10**. The evaporation typically takes from about 20 to 45 minues. When the evaporation process is completed the crucible is permitted to cool off and the finished plate is removed from the bell jar.

FIG. 3 is a bar graph showing the relative sensitivity of plates corresponding to FIGURE 1 and prepared with different proportions of arsenic and iodine or bromine. The sensitivities of a 100 percent selenium plate and a selenium-arsenic plate prepared under similar conditions are also included for reference. Sensitivity was measured by electrostatically charging the various xerographic plates beneath a corona discharge element and then exposing the plates to light for $\frac{1}{25}$ of a second, measuring the relative dissipation of charge by means of an electrometer, and comparing this relative discharge with a selenium control plate. It is apparent from FIGURE 3 that the light sensitivity of xerographic plates prepared with arsenic and iodine exceed those of a control plate made with ordinary selenium. The sensitivity of plates made under similar conditions with 5, 17.5 and 25 percent arsenic and no iodine are included for purposes of comparison. It can be seen that the plates containing iodine exhibits a very substantial increase in sensitivity as compared with the plates lacking iodine. This increase sensitivity may not become apparent until several days after the plate is made. The plate containing the bromine addition shows a sensitivity comparable to plates containing iodine.

As shown in FIGURE 2 in a further embodiment of the invention, it has been found advantageous to deposit the selenium-arsenic-iodine mixture in a thin surface layer layer on the xerographic plate onto a layer of substantially pure selenium. A xerographic plate can be constructed in accordance with this embodiment by including a second evaporation source, such as a molybdenum boat, in the vacuum bell jar. The principal evaporation source is loaded with pure selenium or selenium with iron powder while the selenium-arsenic-iodine mixture is placed in the molybdenum boat which comprises a second evaporation source. The selenium is first evaporated onto a suitable support member **11** exactly as described previously. As soon as the selenium evaporation is completed and without breaking the vacuum in the bell jar, the selenium-arsenic-iodine mixture is evaporated onto the selenium. By confining the arsensic and iodine to a thin surface layer, smaller quantities of these materials can be employed. In addition, the coating process is simplified because the alloy is evaporated in a very short time and there is less concern about non-uniform distribution of the arsenic and iodine in the plate.

Layer **14** may be of any convenient thickness. Layers between about 0.1 and 0.5 micron have been found satisfactory. There is, no upper limit on this thickness, since as layer **14** becomes very thick, the embodiment of FIGURE 2 simply becomes the embodiment of FIGURE 1.

It is apparent that the layered embodiment is capable of producing substantially the same increase in speed as the plate incorporating arsenic and selenium throughout the bulk of the selenium. There is an additional benefit in employing the embodiment of FIGURE 2. All xerographic plates tend to exhibit an increased rate of charge dissipation in darkness after being exposed to bright light. High speed plates tend to exhibit this undesirable property to a greater degree. It has been found that layered plates corresponding to FIGURE 2 exhibit this effect, known as fatigue, to a lesser degree than those corresponding to FIGURE 1. Thus, after exposure to bright light, a selenium plate containing 10 percent arsenic and 100 parts per million of iodine throughout its bulk lost over 90 percent of its charge in 30 seconds. When the

same arsenic-selenium-iodine mixture was confined to a one-half micron surface layer the plate was able to retain more than half its charge after the previous exposure to bright light. It may be noted that these two plates have nearly the same sensitivity.

It has been discovered that the spectral response of xerographic plates in accordance with the present invention is broadened in proportion to the amount of arsenic present, as taught in U.S. Patent 2,803,542 referred to previously. The addition of a halogen on the other hand, increases sensitivity without affecting the spectral response.

The increase in sensitivity for a given selenium plate with increasing amounts of arsenic, with and without a halogen, is shown in FIGURE 4. In FIGURE 4, curve A represents the light sensitivity of a selenium plate with increasing amounts of arsenic, with no halogen additive. The light sensitivity of 1 at 0 percent arsenic would be the sensitivity of a 100 percent selenium plate. As can be seen from curve A, the sensitivity of a selenium-arsenic plate does not show improved sensitivity over a 100 percent selenium plate until the arsenic is added in amounts upward of about 13 percent. On the other hand, curve B shows that the addition of 1000 parts per million of iodine increases the light sensitivity of the selenium-arsenic plate at any percentage of arsenic, reaching a maximum of about 6 times the sensitivity of a 100 percent selenium plate at about 18 percent arsenic.

Iodine is the preferred halogen additive, in that it can be conveniently added as a solid in weighed amounts to arsenic and selenium in a Pyrex vial just prior to evacuation and sealing. As previously described, the vial is then heated in a rocking furnace to insure proper mixing and homogenization.

Inasmuch as the other members of the halogen family are either liquid or gaseous at room temperature, additional precautions should be taken to insure that they are properly combined with the selenium and arsenic.

Bromine is added as liquid drops from a burette to the arsenic and selenium which is precooled in a glass tube by a Dry Ice-acetone mixture. This procedure is important in order to prevent a complete loss of the bromine during evacuation since the melting point of bromine is −7° C.

Chlorine may be added by slightly different procedure. In this procedure the chlorine gas is admitted to an evacuating tube containing gram quantities of arsenic and selenium. The remaining standard amounts of arsenic and selenium are added to the tube and cooled in Dry Ice-acetone mixtures prior to sealing under vacuum. Both the bromine and chlorine are now sufficiently blended with the arsenic and selenium and the mixing and homogenization process is then carried out as set forth in the description using iodine as an additive. It has been found that bromine gives affects similar to iodine when used in the plates of this invention.

The following examples further specifically define the present invention with respect to the method of making the halogen-doped selenium-arsenic plates. The parts and percentages in the disclosure, examples, and claims are by weight unless otherwise indicated. The examples below are intended to illustrate various preferred embodiments of making a halogen-doped selenium-arsenic plate.

EXAMPLE I

A mixture of about 17.5 percent arsenic, about 82.5 percent selenium, plus about 1000 p.p.m. of iodine are sealed in a Pyrex vial and reacted at about 525 C. for about three hours in a rocking furnace. The mixture is then cooled to about room temperature, removed from the Pyrex vial, and placed in a quartz crucible within a bell jar. An aluminum plate is supported about 12 inches above the crucible and maintained at a temperature of about 70° C. The bell jar is then evacuated to a pressure of about 5×10^{-5} torr and the quartz crucible is heated to a temperature of about 380° C. to evaporate the selenium mixture onto the brass plate. The crucible is kept at the evaporation temperature for approximately 30 minutes. At the end of this time the crucible is permitted to cool and the finished plate is removed from the bell jar.

EXAMPLE II

A mixture of about 17.5 percent arsenic and about 82.5 percent selenium are placed in a Prex vial. Bromine is added to this mixture in a concentration of about 500 p.p.m. as liquid drops from a burette to the arsenic and selenium mixture which is precooled in the glass vial by a Dry Ice-acetone mixture. The Pyrex vial containing the resulting mixture is then evacuated and sealed. The sealed Pyrex vial is then treated in the same manner as the iodine-doped mixture set forth in Example I.

EXAMPLE III

A mixture of about 15 percent arsenic and about 85 percent selenium is mixed with chlorine by first placing one gram each of arsenic and selenium in an evacuated tube. Chlorine gas is then admitted to the evacuated tube to produce a concentration of chlorine of about 2,000 p.p.m. The chlorine reacts with the arsenic and selenium as evidenced by the evolution of heat. The remaining amounts of arsenic and selenium are then added to the tube and cooled in a Dry Ice-acetone mixture prior to sealing in the Pyrex vial under vacuum. The sealed Pyrex vial is then treated in the same manner as the iodine-doped mixture set forth in Example I.

The plates made in accordance with the present invention are normally used in a xerographic process including at least the three basic steps of charging, exposing, and developing. A plate, which has preferably been stored in darkness, is given a surface electrostatic charge by being passed under a corona discharge device or the like. A positive potential or charge on the order of several hundred volts is typical. The plate is then exposed to a pattern of light and shadow, as in a camera. This selectively dissipates the charge previously applied and the remaining charge forms a charge pattern conforming to the light pattern. By using the plates of the present invention, substantial shorter exposure times are possible and a wider range of colors may be reproduced due to the increased sensitivity and broadened spectral response of the plates. Finally, the electrostatic pattern is made into a visible reproduction of the light pattern through selective electrostatically controlled deposition of marking material. Apparatus and materials for carrying out these basic xerographic steps are well-known in the art and need not be further described here.

Although special components and proportions have been stated in the above description of the preferred embodiments of the selenium xerographic plate, other suitable materials, as listed above, may be used with similar results. In addition, other materials may be added to the mixture to synergize, enhance, or otherwise modify its properties. For example, the halogen may be conveniently added as a compound or arsenic or selenium. For example, sodium hypochlorite could well be a source of chlorine. This allows all the halogens to be added to the selenium-arsenic mixture as solids, notwithstanding the fact that some halogens occur in their elemental form as a gas or liquid at room temperature.

What is claimed is:

1. A method of making a xerographic plate which comprises vacuum evaporating a mixture of selenium, arsenic and a halogen onto an electrically conductive support member to form a photoconductive alloy layer thereon, said mixture comprising arsenic in the range of about 0.5 to 50 percent by weight, a halogen in a range of about 10 to 10,000 parts per million, with the balance comprising selenium.

2. The method of claim 1 in which the halogen comprises iodine.

3. A method of making a xerographic plate which comprises vacuum evaporating selenium onto an electrically conductive support member to form a vitreous selenium coating thereon, and during the final stages of said evaporation step, evaporating a photoconductive alloy layer onto said vitreous selenium layer, said alloy layer comprising a mixture of selenium, arsenic and a halogen, with said mixture comprising arsenic in the range of about 0.5 to about 50 percent by weight, a halogen in the range of about 10 to 10,000 parts per million, with the balance comprising selenium.

4. The method of claim 3 in which the halogen comprises iodine.

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