

Dec. 9, 1958

R. M. SCHAFFERT
XEROGRAPHIC PLATE

2,863,768

Filed July 5, 1955

2 Sheets-Sheet 1

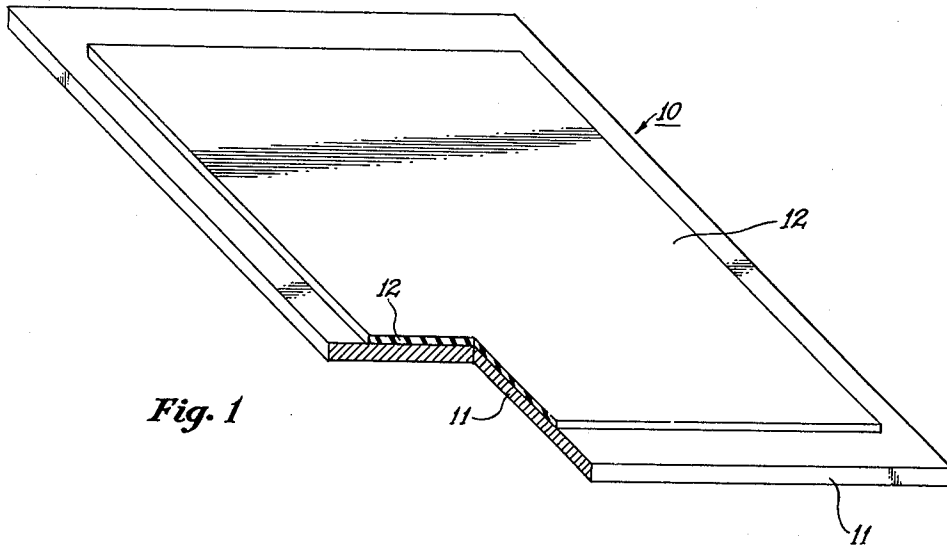


Fig. 1

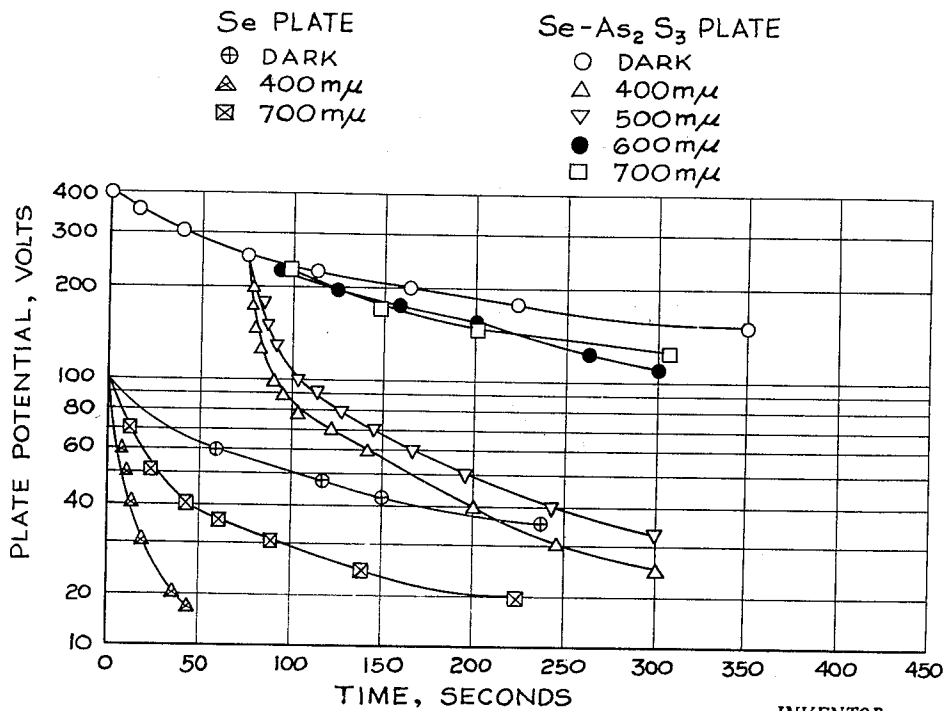


Fig. 2

INVENTOR.
ROLAND M. SCHAFFERT
BY
Frank A. Stenhouse
ATTORNEY

Dec. 9, 1958

R. M. SCHAFFERT
XEROGRAPHIC PLATE

2,863,768

Filed July 5, 1955

2 Sheets-Sheet 2

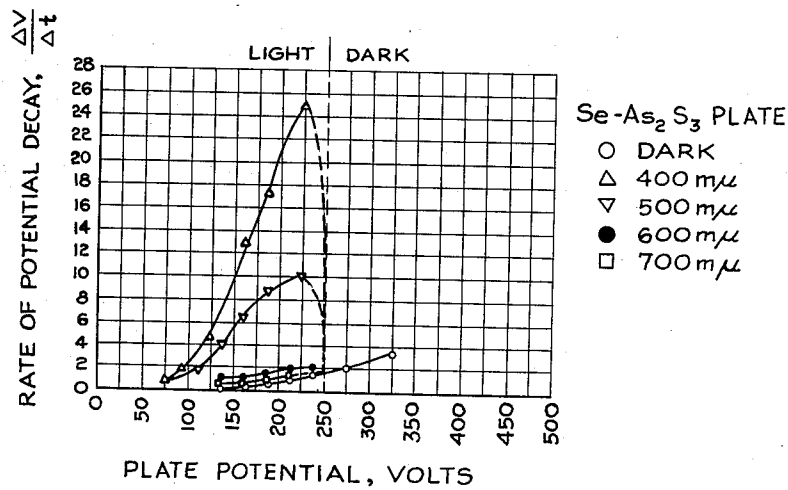


Fig. 3

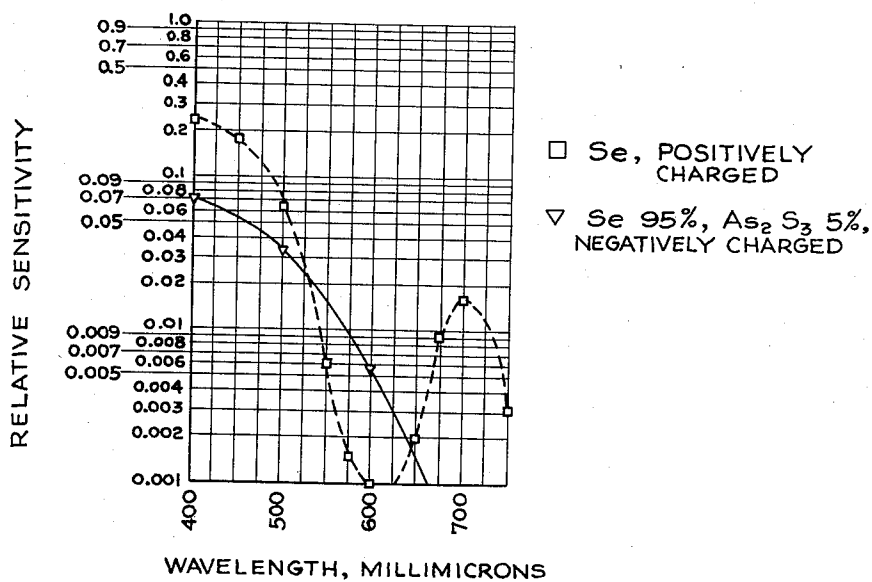


Fig. 4

INVENTOR.
ROLAND M. SCHAFFERT
BY *Frank J. Kunkel*
ATTORNEY

1

2,863,768

XEROGRAPHIC PLATE

Roland M. Schaffert, Columbus, Ohio, assignor, by mesne assignments, to Haloid Xerox Inc., Rochester, N. Y., a corporation of New York

Application July 5, 1955, Serial No. 520,078

12 Claims. (Cl. 96—1)

This invention relates in general to the art of electrophotography, now known as "xerography," and, in particular, to a sensitive plate therefor. More specifically, the invention relates to a new xerographic or electrophotographic member comprising a conductive backing having on at least one surface thereof a photoconductive insulating coating consisting of a mixture of selenium and arsenic trisulfide, which member is known as a "xerographic plate."

In the art of xerography it is usual to form an electrostatic latent image on a member or plate which comprises a conductive backing member such as, for example, a metallic surface 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 a charge when exposed to a light pattern.

Such a plate, while largely sensitive to light in the blue-green spectral range, also has appreciable sensitivity to light in the red spectral range. Thus, once the plate is sensitized as by applying an electrostatic charge thereto, it is necessary to handle the plate in complete darkness to prevent unwanted dissipation of the charge. Furthermore, the loss of potential when stored in the dark (termed "dark decay") for a negative charge is relatively rapid. For this reason, selenium plates are generally used only with positive charging.

Now, in accordance with the present invention, it has been found that an improved xerographic plate can be prepared by incorporation in the photoconductive insulating coating of a minor amount of arsenic trisulfide. The plate, as thus modified, while retaining high sensitivity in the blue-green spectral range, is characterized by an extremely low sensitivity in the red spectral range permitting the handling and developing of such a plate in red light. Furthermore, such plates have a satisfactory dark decay rate for negative charging, combined with high sensitivity to blue-green light.

In general, the permissible range of concentration or proportion of arsenic trisulfide in the selenium layer is relatively broad and may extend from about 0.5% to about 20% and preferably, lies in the range of about 1% to about 10% by weight.

The new and improved plates of the present invention can be prepared by a variety of methods. For example, selenium and arsenic trisulfide in the desired proportions may be mixed and, in molten form, sprayed on the desired surface, or they may be evaporated onto the plate under high vacuum as from a mixture in a single evaporation source or optionally from two separate sources operating to volatilize their contents at the desired speed ratio. Likewise, the mixed ingredients may be placed in a suitable film-forming binder and applied to the surface in the form of a selenium-arsenic trisulfide lacquer. If desired, a transparent insulating coating, as of a vinyl resin, a cellulose ether or ester, a silicone resin, etc.,

2

may be coated on top of the xerographic plate to protect the surface thereof from abrasion and mechanical damage.

In the drawings,

Fig. 1 is an oblique view, partially in section, of a xerographic plate according to one embodiment of the invention.

Fig. 2 is a graph showing the relationship of plate potential to potential decay of a selenium plate as compared to a selenium-arsenic trisulfide plate.

Fig. 3 is a graph showing the relationship of the rate of potential decay to plate potential for a selenium-arsenic trisulfide plate.

Finally, Fig. 4 is a graph showing the spectral sensitivity of a selenium-arsenic trisulfide plate.

In Fig. 1 the xerographic plate 10 consists of a conductive backing member 11 having thereon a coating 12 of selenium and arsenic trisulfide.

The general scope and nature of the invention having been set forth, the following examples are given as typical illustrations of methods by which the desired plates may be prepared.

A brass plate was polished with Glass Wax (a trade name of the Gold Seal Company, Bismarck, North Dakota, for a composition comprising about 75% water, 15% naphtha, 7.5% abrasive, and the balance ammonia, emulsifier, and coloring agent), rinsed in isopropyl alcohol and then degreased in hot isopropyl alcohol vapor. The plate was then attached to a platen about four inches above a molybdenum boat. Six grams of selenium were placed in the boat and a bell jar placed over the apparatus. The system was then evacuated to a pressure of approximately 0.4 micron. Heat was applied to the plate to maintain the brass plate at a temperature of about 80° C. and the selenium deposited on the brass plate while this base plate temperature was maintained.

A mixture of 10 grams of selenium shot was melted in a porcelain crucible over a gas flame and 0.5 gram of arsenic trisulfide added, a little at a time with stirring, until completely dissolved. This produced a mixture consisting of 95.24% selenium and 4.76% arsenic trisulfide. The molten mixture was then poured onto a cold brass plate. When cool, the solidified mixture was broken into small fragments in a mortar. A brass plate was cleaned and attached to a platen as above described. Six grams of the selenium-arsenic trisulfide mixture were placed in a molybdenum boat. A bell jar then enclosed the system, which was evacuated to a pressure 0.4 micron. The platen was heated to maintain the brass plate at a temperature of about 80° C. during deposition. The thickness of the films on the selenium and selenium-arsenic trisulfide plates were measured. The selenium film was 50 microns thick and the selenium-arsenic trisulfide film was 48 microns thick.

The plates were placed in the dark and charged negatively by corona emission. The amount of charge on the plate was then measured with an electrometer. The plates were kept in the dark for some time during which several measurements were made of the charge on the plate to determine the dark decay taking place. In the case of the selenium plate, the corona unit actually imparted a relatively high charge to the plate, but the dark decay was so rapid that it had fallen off to 100 volts before it could be measured. In the case of the selenium plate, because of the rapid dark decay, exposure to light and measurement of the potential on the plate was carried out as soon as possible after charging. In the case of the selenium-arsenic trisulfide plate, the plate was kept in the dark until the potential had fallen to 250 volts. At that point the light was turned on and measurements of potential continued over a period of time to determine the decrease of potential with different wave lengths of

3

light. The light intensity for all wave lengths used on the selenium-arsenic trisulfide plate was 0.03 microwatt per square centimeter. For the selenium only plate, the same light intensity was used for 400 millimicrons wave length. In measuring the light decay for 700 millimicrons wave length, however, a light intensity of 2.34 microwatts per square centimeter was used. These data are plotted in the graph in Fig. 2. As can be seen, the light decay of the selenium-arsenic trisulfide plate for red light (700 millimicrons) is only slightly faster than is the case for the dark decay rate.

The graph in Fig. 3 is derived directly from the graph in Fig. 2, except that a light intensity of 0.03 microwatt per square centimeter was used to determine the light decay for 700 millimicrons wavelength. Only the values for the $\text{Se-As}_2\text{S}_3$ plate were plotted in Fig. 3. For the different potential values,

$$\frac{\Delta V}{\Delta t}$$

was determined by measuring the differences on each axis between adjacent points on the potential decay curves. These values of

$$\frac{\Delta V}{\Delta t}$$

were then plotted against the plate potential to give the required curves. The curves show very clearly how the total current through the plate changes when, as the potential on the plate is decaying in the dark, the plate is exposed to light. The photo current is determined by the difference between the current when the light is on and the dark current. As can clearly be seen from these curves, the selenium-arsenic trisulfide plate possesses a high degree of light sensitivity for negative charging.

Using these same data, the spectral sensitivity of the plates was also plotted, as set forth in the graph in Fig. 4. For these computations the standard method was adopted of using the reciprocal of the time for the potential to drop from 200 to 100 volts with a light intensity of 0.03 microwatt per square centimeter. A dark decay correction was applied to these computations. The formula used was

$$S = \frac{t_D - t_L}{t_D t_L}$$

Where S equals sensitivity, t_D is the time in seconds for the potential drop of 200 to 100 volts and t_L is the time for the same drop when the plate is exposed to light. For very slow dark decay, the dark decay correction can be neglected.

As can be seen in Fig. 4, compared with selenium the selenium-arsenic trisulfide plate negatively charged is more sensitive at 600 millimicrons (yellow light) but less sensitive in the blue-green region than selenium that is positively charged. Its sensitivity falls to near 0 at 700 millimicrons (red light). The overall sensitivity of this plate to white light is estimated to be about one-half that of selenium positively charged.

The selenium used in the preparation of xerographic plates should be free of impurities such as copper, iron, lead, and bismuth, which appear to adversely affect its ability to hold electrostatic charges, that is by forming conducting paths in the film or promoting the formation of conducting hexagonal selenium so that electrostatic charges leak off rapidly even in the dark and electrostatic deposition of powder or other finely-divided material cannot be obtained. Preferably, there should be used amorphous selenium available in pellet form $\frac{1}{16}$ inch to $\frac{1}{8}$ inch size under the name "A. R. Q." (ammonia reduced in quartz from selenium oxide) as manufactured, for this grade of selenium is essentially pure, containing less than about twenty parts per million of impurities. If purified, other grades of selenium, i. e. "D. D. Q." (double distilled in quartz) and "C. C. R." (commercial grade) as manufactured can likewise be employed in the process

4

disclosed herein. To purify these grades of selenium, they are first freed of copper, iron, lead, and bismuth by distillation. The selenium is next heated to about 250° C., slightly above its melting point, and, while molten, is then dropped through a shot tower (or in the laboratory by means of an eye dropper) into water to form pellets. The pellets are subsequently treated with petroleum ether to remove water and allowed to air dry. If desired, the purified selenium can be remelted and cast in boats to form sticks. It can also be reduced in size by grinding or micropulverizing to facilitate melting and mixing with the arsenic trisulfide. Where the plates are prepared either by vacuum evaporation of the selenium and arsenic trisulfide or by spraying in molten form, it is desirable that the base plate be pre-heated to a temperature of at least about 75° C.

A conductive base plate is usually required for xerographic plates and metal forms the most suitable material. However, a high conductivity is not required and almost any structurally satisfactory material which is more conductive than the selenium-arsenic trisulfide layer can be used. Materials having electrical resistivities about 10^{10} ohm-centimeter are generally satisfactory for the base plates of this invention although it is more desirable to use materials of less than about 10^5 ohm-centimeter. Any gross surface irregularities, i. e. burns, tool marks, are removed from the base plate by grinding or polishing, although it is unnecessary to polish the plate until it has a mirror-like surface. The plate surface is cleaned before coating with the selenium-arsenic trisulfide in order to remove grease, dirt, and other impurities which might prevent firm adherence of the coating to the base plate. This is readily accomplished by washing the plate with any suitable alkali cleaner or with a hydrocarbon solvent, such as benzene, followed by rinsing and drying. Suitable base plate materials are aluminum, glass having a conductive coating thereon as of tin oxide or aluminum, stainless steel, nickel, chromium, zinc, and steel, which do not react with the selenium or arsenic trisulfide to produce undesirable compounds such as oxides, nor promote the formation of hexagonal selenium and thereby adversely affect the electrophotographic qualities of the film.

Also, conductive plastic, conductively coated paper, or other web or film-like member may be used as the conductive supporting surface as desired. It is to be understood that the backing member selected for this plate may be in the form of a flat plate or may equally be in the form of a cylinder, flexible sheet, or other member having a surface suitable for the xerographic process.

While the plate of this invention has been discussed chiefly in terms of its utility when negatively charged, novel and unusual advantages may be obtained by using a positive charge to sensitize the plate. Selenium-arsenic trisulfide plates apparently exhibit n-type conduction. When positively charged the plates have little sensitivity to visible light. However such plates have definite advantages for xeroradiography where insensitivity to visible light is desirable. As X-rays are absorbed throughout the film, electrons released deep within the film would move toward a positively charged surface. Thus the plates positively charged would be light insensitive, X-ray sensitive.

I claim:

1. As an article of manufacture a xerographic plate comprising an electrically conductive backing member having on at least one surface a layer of photoconductive insulating material consisting essentially of a substantially uniform mixture of between about 0.5% and about 20% by weight of arsenic trisulfide and the remainder substantially vitreous selenium.

2. A xerographic plate according to claim 1 in which the photoconductive insulating material has between about 1% and about 10% by weight of arsenic trisulfide and the remainder substantially vitreous selenium.

5

3. A xerographic plate according to claim 1 in which the electrically conductive backing member is a metal surface.

4. A xerographic plate according to claim 1 in which the photoconductive insulating material is between about 1% and about 10% by weight of arsenic trisulfide and the remainder substantially vitreous selenium and the electrically conductive backing member is an aluminum surface.

5. A xerographic plate according to claim 1 in which the photoconductive insulating layer is between about 1% and about 10% by weight of arsenic trisulfide and the remainder substantially vitreous selenium and the electrically conductive backing member is a brass surface.

6. A process of producing a xerographic reproduction wherein an electrostatic image is formed on a photoconductive insulator, the steps comprising placing a negative electrostatic charge on the photoconductive insulating surface of a xerographic member comprising an electrically conductive backing member having thereon a photoconductive insulating layer of a substantially uniform mixture of between about 0.5% and about 20% by weight of arsenic trisulfide and the remainder substantially vitreous selenium and selectively dissipating electrostatic charge from the photoconductive insulating surface of said xerographic member by exposing the charged surface to an image pattern of light having a wave length of less than about 650 millimicrons.

7. A process of producing a xerographic reproduction wherein an electrostatic image is formed on a photoconductive insulator, the steps comprising placing a positive electrostatic charge on the photoconductive insulating surface of a xerographic member comprising an electrically conductive backing member having thereon a photoconductive insulating layer of a substantially uniform mixture of between about 0.5% and about 20% by weight of arsenic trisulfide and the remainder substantially vitreous selenium and selectively dissipating electrostatic charge from the photoconductive insulating surface of said xerographic member by exposing the charged surface to an image pattern of light having a wave length of less than about 650 millimicrons.

8. A process of producing a xerographic reproduction wherein an electrostatic image is formed on a photoconductive insulator, the steps comprising placing a negative electrostatic charge on the photoconductive insulating surface of a xerographic member comprising an electrically conductive backing member having thereon a photoconductive insulating layer of a substantially uniform mixture of between about 0.5% and about 20% by weight of arsenic trisulfide and the remainder substantially vitreous selenium, selectively dissipating electrostatic charge from the photoconductive insulating surface of said xerographic member by exposing the charged surface to an image pattern of light having a wave length of less than about 650 millimicrons and developing the resulting electrostatic image with positively charged powder particles.

9. A process of producing a xerographic reproduction wherein an electrostatic image is formed on a photoconductive insulator, the steps comprising placing a negative electrostatic charge on the photoconductive insulating surface of a xerographic member comprising an electrically conductive backing member having thereon a photoconductive insulating layer of a substantially uniform mixture of between about 1.0% and about 10% by weight of arsenic trisulfide and the remainder substantially vitreous selenium and selectively dissipating electrostatic charge from the photoconductive insulating surface of said xerographic member by exposing the charged surface to an image pattern of light having a wave length of less than about 650 millimicrons.

6

ous selenium and selectively dissipating electrostatic charge from the photoconductive insulating surface of said xerographic member by exposing the charged surface to an image pattern of light having a wave length of less than about 650 millimicrons.

10. A process of producing a xerographic reproduction wherein an electrostatic image is formed on a photoconductive insulator, the steps comprising placing a positive electrostatic charge on the photoconductive insulating surface of a xerographic member comprising an electrically conductive backing member having thereon a photoconductive insulating layer of a substantially uniform mixture of between about 1.0% and about 10% by weight of arsenic trisulfide and the remainder substantially vitreous selenium and selectively dissipating electrostatic charge from the photoconductive insulating surface of said xerographic member by exposing the charged surface to an image pattern of light having a wave length of less than about 650 millimicrons.

11. A process of producing a xerographic reproduction wherein an electrostatic image is formed on a photoconductive insulator, the steps comprising placing a negative electrostatic charge on the photoconductive insulating surface of a xerographic member comprising an electrically conductive backing member having thereon a photoconductive insulating layer of a substantially uniform mixture of between about 1.0% and about 10% by weight of arsenic trisulfide and the remainder substantially vitreous selenium, selectively dissipating electrostatic charge from the photoconductive insulating surface of said xerographic member by exposing the charged surface to an image pattern of light having a wave length of less than about 650 millimicrons and developing the resulting electrostatic image with positively charged powder particles.

12. A process of producing a xerographic reproduction wherein an electrostatic image is formed on a photoconductive insulator, the steps comprising placing a positive electrostatic charge on the photoconductive insulating surface of a xerographic member comprising an electrically conductive backing member having thereon a photoconductive insulating layer of a substantially uniform mixture of between about 0.5% and about 20% by weight of arsenic trisulfide and the remainder substantially vitreous selenium, selectively dissipating electrostatic charge from the photoconductive insulating surface of said xerographic member by exposing the said member to an X-ray image pattern and developing the resulting electrostatic image with electrically charged powder particles.

References Cited in the file of this patent

UNITED STATES PATENTS

2,199,104	Johnson et al. Apr. 30, 1940
2,297,691	Carlson Oct. 6, 1942
2,575,392	Peters et al. Nov. 20, 1951
2,657,152	Mengali et al. Oct. 27, 1953
2,662,832	Middleton et al. Dec. 15, 1953
2,692,178	Grandadam Oct. 19, 1954

FOREIGN PATENTS

284,942	Great Britain Feb. 9, 1928
358,672	Great Britain Oct. 15, 1931

OTHER REFERENCES

Mellor: Treatise on Inorganic and Theoretical Chemistry, 1929; vol. 9; page 274.