

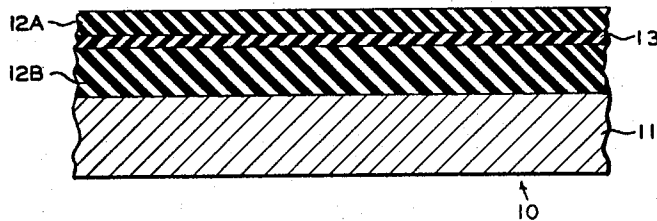
Nov. 29, 1960

R. M. SCHAFFERT

2,962,376

XEROGRAPHIC MEMBER

Filed May 14, 1958



INVENTOR.

Roland M. Schaffert

BY

George W. F. Simmons

ATTORNEY

1

2,962,376

XEROGRAPHIC MEMBER

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

Filed May 14, 1958, Ser. No. 735,302

8 Claims. (Cl. 96—1)

This invention relates in general to xerography and in particular to a light sensitive plate therefor.

In the xerographic process which was first presented in U.S. 2,297,691 to C. F. Carlson, a photoconductive insulating surface on a relatively low electrical resistance backing is electrostatically charged in the dark, and then exposed to a light image. The charges leak off rapidly to the backing in proportion to which any given area is exposed. After such exposure the coating is contacted with electrostatically charged marking particles in the dark. These particles adhere to the areas where the electrostatic charges remain forming a powder image corresponding to the electrostatic image. The powder image can then be transferred to a sheet of transfer material resulting in a positive or negative print as the case may be having excellent detail and quality. Alternatively, where the base plate is relatively inexpensive, as of paper or plastic, it may be desirable to fix the powder image directly to the plate itself. The present invention has as its scope and purpose the provision of a new sensitive member particularly useful in and adapted to xerography.

The photoconductive insulating coatings originally disclosed by Carlson comprised anthracene, sulphur, and various mixtures of these materials as sulphur with selenium, etc. These materials have relatively low light sensitivity. Consequently, there was an urgent need for improved photoconductive insulating materials. The discovery of the photoconductive insulating properties of highly purified vitreous selenium has resulted in this material becoming the standard in commercial xerography. The photographic speed of this material is many times that of the prior art photoconductive insulating materials. However, its spectral response is very largely limited to the blue or near ultraviolet. Most light sources such as incandescent, photoflood, and sunlight have an appreciable if not major portion of their radiation in the red and far red portions of the spectrum. Thus, although vitreous selenium is enormously faster than prior art photoconductive insulating materials, it uses only a small portion of the available radiant energy. Further, in many copying applications, as the reproduction of documents having printing, writing, or other information thereon in blue, or in making a color reproduction of a natural scene, the inability of vitreous selenium to "see" larger wavelengths places a severe limitation on the utility of the vitreous selenium in the xerographic process. Now, in accordance with this invention there has been found a xerographic sensitive member, known as a xerographic plate, which makes full use of the excellent sensitivity of vitreous selenium in the blue and near ultraviolet together with its highly insulating qualities in the dark while imparting significant sensitivity in the red. The novel plate of the instant invention comprises a conductive backing member having thereon a layer of vitreous selenium having therein a layer of a red sensitive photoconductor. It has been found that the coefficient of absorption in vitreous selenium falls off sharply for radiation having a wavelength greater than about 600 millimicrons, that is, radiation

2

having a shorter wavelength is absorbed in the very top-most layer of the selenium exposed to the incident radiation. Radiation having a longer wavelength, particularly red light, penetrates for a considerable distance into the selenium before it is absorbed. Radiation of this wavelength, that is, red light, does not have sufficient energy to raise an electron to the conduction band in vitreous selenium. Accordingly, its absorption adds nothing to the sensitivity of the selenium plate.

In the plate of the instant invention a layer of a red sensitive photoconductor is positioned in the selenium layer within the range of penetration therein of red light. On exposure to activating radiation the light having a wavelength shorter than about 600 millimicrons is absorbed on or close to the top-most layer of vitreous selenium overlying the layer of red sensitive photoconductor generating hole-electron pairs therein. The red light, penetrating to a greater depth, generates hole-electron pairs in the layer of red sensitive photoconductor thus also contributing to the overall light response.

The plate of the instant invention has the red sensitive photoconductor positioned in the selenium layer—i.e., there is a layer of vitreous selenium both under and above the red sensitive photoconductor. This is illustrated in the drawing. The figure is a diagrammatic representation in section of an improved xerographic member according to this invention. In the figure there is shown a new xerographic member 10 comprising an electrically conducting backing 11 having a layer of vitreous selenium 12 thereon, which is divided into a top layer 12A and a bottom layer 12B by an interlayer therein of a red sensitive photoconductor 13. By presenting a layer of vitreous selenium to receive the sensitizing charges placed on the free surface of the photoconductive layer in the normal xerographic process, full use is made of the excellent insulating properties in the dark of vitreous selenium thereby preventing smudging or oblivation as by lateral conductivity while positioning a layer of vitreous selenium between the red sensitive photoconductor and the conductive backing material utilizes the excellent insulating properties of vitreous selenium to prevent injection of charge carriers from the backing material as will be explained more fully hereafter. Thus the xerographic member according to this invention employs a red sensitive photoconductor (which materials generally are substantially less electrically insulating than vitreous selenium) without any substantial increase in dark decay therefrom.

These novel xerographic members are further characterized by an increased sensitivity to light and particularly as evidenced by a change in sensitivity specifically characterized by a substantially increased photoconductive response to red light, i.e., radiation having a wavelength greater than about 600 millimicrons. Further objects and features of the invention will become evident in the following description of the invention.

The backing member is selected according to conventional requirements for the xerographic art and generally comprises a metallic plate, cylinder, sheet, web or the like, or other backing material having structural characteristics and being electrically conductive either by its inherent nature or by having an electrically conductive material dispersed throughout its volume or coated thereover. Suitably this backing member may be a metallic member such as a member of aluminum, brass, magnesium, zinc, iron, steel, chromium or the like, or may be of other electrically conductive material such as electrically conductive glass (as glass coated with tin oxide, indium oxide, or copper iodide), metallized paper or plastic, or the like, or electrically conductive resins, plastics or like materials. According to a presently preferred embodiment of the invention, the backing member consists of

3

an aluminum plate or cylinder having a thin coating thereover of an aluminum oxide layer. Where it is desired to expose the photoconductive insulating layer 12 through the backing material 11, thereby necessitating the use of a transparent conductive backing, a particularly preferred backing comprises glass having a coating thereon of tin oxide rendering the coated surface electrically conductive.

Coated on at least one surface of the base member is the photoconductive insulating layer comprising a first layer of vitreous selenium 12B, then a thin layer of the red sensitive photoconductor 13, and then disposed on the surface of the red sensitive photoconductor another layer of vitreous selenium 12B. The layer of red sensitive photoconductor 13 is so positioned relative to the surface receiving the incident radiation as to be no more than about 20 microns from the surface thereof. Thus, if exposure is to be from the free surface of the vitreous selenium, the layer of red sensitive photoconductor desirably is no more than about 20 microns beneath the free surface. Conversely, if exposure is to be through the backing member 11 then the layer of red sensitive photoconductor is no more than about 20 microns from the interface between the vitreous selenium and the conductive backing member. It has been found that the light absorption of amorphous selenium is such that red light does not penetrate in any substantial amount to more than about 20 microns. Accordingly, in order for a significant amount of activating radiation to penetrate to the layer of red sensitive photoconductor, layer 13 should not be separated by more than about 20 microns of vitreous selenium from the activating radiation.

The conductive backing, by virtue of its being an electrical conductor, constitutes an almost infinite supply of charge carriers relative to the vitreous selenium. Accordingly, when exposure is to occur through the back, two considerations regulate the thickness of layer 12B: First, depending on the relative electron energy levels of the conductive backing, the selenium and the red sensitive photoconductor, the red sensitive photoconductor may cause undesirable injection of charge carriers into the bulk of the selenium of not sufficiently separated from the conductive backing. Thus, if the red sensitive photoconductor is an n-type material (that is, has a larger number of negative charge carriers than positive charge carriers) and positive charges are used to sensitize the selenium, the red sensitive photoconductor will cause injection of electrons into the selenium thereby decreasing the ability of the vitreous selenium to retain an electrostatic charge in the dark unless layer 12B effectively separates layer 13 from backing 11. Secondly, as stated above, layer 12B should be no thicker than about 20 microns when, as here, exposure is to be through the backing. For exposure through the back, then, layer 12B should be from about 0.1 to 20 microns thick and preferably is from about 1 to 10 microns thick while layer 12A is thick enough to afford sufficient charge storage for utility in the xerographic process, i.e., so that the thickness of the overall photoconductive insulating layer is at least about 20 microns.

It has been found that while red light will penetrate vitreous selenium to an appreciable distance, blue light (to which vitreous selenium responds) is highly absorbed by the red sensitive photoconductor. Consequently, if there is no layer of vitreous selenium intervening between the red sensitive photoconductor and the backing material while the red light falling on the red sensitive photoconductor is effective to create hole-electron pairs in response thereto, little or not use is made of the shorter wavelength radiations which are largely absorbed by the red sensitive photoconductor without the corresponding creation of hole-electron pairs thereby. Thus, the use of a red sensitive backing layer coupled with exposure through the back merely acts to substitute a red sensitive plate for the previously blue sensitive plate

4

whereas the plate of the instant invention creates a xerographic plate responding to both the red and the blue portions of the spectrum.

Where exposure of the xerographic plate occurs through the free surface of the vitreous selenium, the red sensitive photoconductor may be as close to the free surface of the vitreous selenium as desired so long as it does not interfere with the charge-holding capacities of the selenium. In general, it has been found desirable that the red sensitive photoconductor should be covered with at least about one micron of vitreous selenium. It is preferred that the thickness of layer 12B be from about 2 to about 10 microns.

The red sensitive photoconductive materials which appear operable to constitute layer 13 in the xerographic member of the instant invention consist of the sulfides, selenides and/or tellurides of antimony, arsenic, bismuth, cadmium, gallium, indium, lead, mercury and tellurium. While thallium has the requisite red sensitivity, it has been found that elemental thallium causes undesirable crystallization in the selenium. Layer 13 may be formed by interrupting the vacuum evaporation of the selenium after the deposition of layer 12B and depositing the desired red sensitive photoconductor, then continuing the evaporation of the selenium. Alternatively, the layer may be formed by evaporating the desired compound during the evaporation of the selenium, timing the evaporation of the red sensitive photoconductor relative to the selenium (as by means of a shutter over the boat or boats containing the desired compound or compounds) to assure the deposition of layers 12B and 12A of vitreous selenium. If desired the metal may be evaporated as such to form the selenide with the coevaporated selenium; or a mixed seleno-sulfide and/or telluride may be formed by coevaporation of sulfur and/or tellurium with the metal and selenium. In this case stoichiometric equivalence is not essential, particularly in the case of the arsenic and tellurium. The layer of red sensitive photoconductor is usually in the order of 0.5 to 10 microns thick.

The total thickness of the layer of photoconductive insulator should be from about 20 to 200 microns. Generally it is preferred that the photoconductive layer be from about 20 to about 80 microns thick. Thus, the xerographic plate according to the instant invention comprises a conductive backing material having on at least one surface thereof a layer of vitreous selenium from about 20 to 200 microns thick, said selenium having therein a layer of red sensitive photoconductor at least about 1 micron from the surface of the selenium layer receiving the activating radiation and no more than about 20 microns from that surface.

The preferred method of preparation of xerographic plates according to the instant invention is by vacuum evaporation. In this process the backing member, as an aluminum plate, is placed in a high vacuum (in the order of about 1 micron of mercury pressure) and a layer of vitreous selenium evaporated thereon while maintaining the backing plate at a temperature of between about 60° and 90° C. and preferably in the order of about 75° C. The deposition of the selenium layer is halted, as by placing a shutter over the evaporation boat, when the layer reaches the desired thickness. The layer of red sensitive photoconductor is then evaporated onto the surface from a second evaporation source. When the evaporation of the red sensitive photoconductor is completed, the evaporation of the selenium is resumed and continued until the desired thickness of selenium has been deposited. The layer of red sensitive photoconductor is thinner than the vitreous selenium carrier layer and may be as thin as 0.1 micron or as large as 50 percent of the thickness of the selenium. It is usually not less than about 1 micron and no more than about 20 percent of the thickness of the selenium layer. Desirably, it will be between about 0.5 and 10 microns thick. Other

5

methods of preparation of the new xerographic member according to this invention may be employed than the presently preferred method and the following examples are presented in illustration of but not in limitation of the invention.

Example 1

A brass plate having a smooth, flat surface is totally cleaned by scrubbing in water containing a detergent. The plate is rinsed clean and is then polished with a cleaning material which is understood and believed to have a hydrocarbon wax base and being available under the trade name "Glass Wax." This polish is applied uniformly over the surface of the plate and is vigorously polished off using a clean dry cloth to leave a polished surface which is understood and believed to have an extremely thin layer of a hydrocarbon wax material. The thus prepared plate is placed in an evacuation chamber in contact with a platen through which is circulated water at a controlled temperature. The chamber is evacuated and the water temperature set to control the temperature of the brass plate at 80° C. Selenium placed in a molybdenum evaporation boat is then brought to a position about 6" from the surface of the plate, and the selenium evaporated onto the surface by heating from electrical heaters located at the molybdenum evaporation boats. A shutter is then drawn over the boat to stop the evaporation when the selenium is about 15 microns thick and another molybdenum evaporation boat moved into evaporation position. A layer of mercuric sulfide about 2 microns thick is evaporated. This boat is then shuttered, and the evaporation of the selenium continued to completion placing an additional layer of vitreous selenium about 7 microns thick on the plate. After the evaporation is completed the plate is removed from the evaporation chamber. The plate so prepared is suitable for xerography and characterized by having extended spectral response.

Example 2

An aluminum plate having a thin coating thereover of an aluminum oxide layer is placed in the evaporation chamber used in Example 1 in contact with the platen thereof. No water is circulated in the platen. The selenium is evaporated from an Alundum (a trademark of the Norton Co., for an alumina refractory) boat. After evaporation proceeds for about 25 minutes, the shutter is removed from a second Alundum crucible and tellurium evaporated while the evaporation of the selenium proceeds. The boat containing the tellurium is heated before the shutter is removed, the shutter preventing the premature escape of the tellurium vapors. The rate of evaporation of the tellurium relative to selenium is such that the layer formed during the coevacuation is estimated to contain about 45 percent tellurium based on the total weight of the selenium and tellurium being evaporated at that time. After two minutes the shutter is replaced on the tellurium-containing boat, and the evaporation of the selenium completed five minutes thereafter. The resulting xerographic plate has a photoconductive layer having a total thickness of about 50 microns. It is estimated, based on the evaporation rate, that the thickness of the selenium-tellurium layer is about 3.5 microns while the selenium coating thereover is about 5 microns thick. After the evaporation is completed the plate is removed from the vacuum chamber. The plate so prepared is suitable for xerography and is particularly characterized by having greatly extended spectral response as compared to xerographic plates containing only vitreous selenium.

Example 3

The procedure of Example 2 was repeated employing indium trisulfide in the second boat which is evaporated while the evaporation of the selenium continues. The total thickness of the photo-conductive insulating layer is again about 50 microns, the thickness of the layer con-

6

taining the indium trisulfide is about 8 microns and the thickness of the overlying selenium layer about 2 microns. The percentage of indium trisulfide in the red sensitive photoconductive layer is about 18%. The thus produced plate is characterized by increased xerographic sensitivity to red light.

Example 4

The procedure of Example 2 is repeated using gallium in place of tellurium. Layer 12B is about 20 microns, layer 12A about 3 microns and layer 13 about 1 micron. The evaporation of gallium is controlled to give a concentration of 80-85% gallium triselenide by weight in layer 13. A plate of comparable quality and utility is produced.

Example 5

The procedure of Example 1 is repeated using antimony trisulfide for the red sensitive photoconductor. A plate of comparable quality is produced.

The use of the red sensitive photoconductive layer in the midst of the vitreous selenium causes the creation of both holes and electrons upon the absorption of activating radiation, i.e., red light. Under the electrostatic field applied across the layer of vitreous selenium by reason of the sensitizing charges thereon, both the holes and electrons migrate through the vitreous selenium. It has been found that selenium layers conduct both electrons and holes but that the mobility for holes is approximately ten times that for electrons. Thus, before vitreous selenium can be used in the novel plates of the instant invention it should be treated to increase the range therein of the minority charge carriers.

It is presently believed that in vitreous selenium, the selenium forms long chains with an unpaired electron at each end. This unpaired electron creates a possible electron trap. If two or more selenium chains terminate in the same area, the result is likely to be a fairly deep electron trap. Under favorable circumstances, oxygen and selenium are isomorphous. If one of the chains terminates in oxygen, the trap is likely to be deeper due to the more electronegative character of oxygen. Accordingly, it has been found that if selenium is treated with an oxygen acceptor, and particularly one possessing two free (i.e., valence) electrons, the material acts to remove oxygen and may also supply the need of the unpaired electron in the selenium chain thus "filling" the trap. A satisfactory process for accomplishing this has been found to be adding iron filings to a crucible containing pellets of xerographic grade selenium and evaporating the selenium under vacuum at a temperature well below the boiling point of iron. Such a treatment "fills" the trap sites in the vitreous selenium to such an extent as to impart a long range to electrons.

Xerographic members such as the ones above described may be used in the xerographic process with either positive or negative polarity charging, generally to a potential in the order of about 100 to 800 volts, followed by exposure to an optical image whereby there is selective dissipation of the electrostatic charge. The resulting electrostatic image can be developed, i.e. made visible, by treatment with an electroscopic material and optionally the developed image is transferred to a support member to yield a xerographic print.

It is to be understood that other methods of preparation of the xerographic member may be employed including melting and pressing or spraying molten selenium and/or red sensitive photoconductor onto the appropriate carrier layer.

I claim:

1. A xerographic plate comprising an electrically conductive backing member having on at least one surface a layer of photoconductive insulating material between about 20 and 200 microns thick, said material consisting essentially of vitreous selenium and having therein a layer between about 0.5 and 10 microns thick of a red

7

sensitive photoconductor, said photoconductor being positioned within the selenium at least about 0.1 micron from said backing material and at least about 1 micron from the free surface of said selenium layer and no more than about 20 microns from the surface of the selenium receiving the activating radiation.

2. A xerographic plate comprising an electrically conductive backing member having on at least one surface a layer of photoconductive insulating material between about 20 and 200 microns thick, said material consisting essentially of vitreous selenium and having therein a layer between about 0.5 and 10 microns thick of a red sensitive photoconductor selected from the group consisting of the sulfides, selenides and tellurides of antimony, arsenic, bismuth, cadmium, gallium, indium, lead, mercury, tellurium and mixtures thereof with each other and with vitreous selenium, said photoconductor being positioned within the selenium at least about 0.1 micron from said backing material and at least about 1 micron from the free surface of said selenium layer and no more than about 20 microns from the surface of the selenium receiving the activating radiation.

3. A xerographic plate comprising an electrically conductive backing member having on at least one surface a layer of photoconductive insulating material between about 20 and 200 microns thick, said material consisting

8

essentially of vitreous selenium and having therein a layer between about 0.5 and 10 microns thick of a red sensitive photoconductor selected from the group consisting of the sulfides, selenides and tellurides of antimony, arsenic, bismuth, cadmium, gallium, indium, lead, mercury, tellurium and mixtures thereof with each other and with vitreous selenium, said photoconductor being at least about 2 microns within said vitreous selenium and no more than about 10 microns from the surface of the selenium receiving the activating radiation.

4. A xerographic plate according to claim 3 wherein said red sensitive photoconductor is tellurium selenide.

5. A xerographic plate according to claim 3 wherein said red sensitive photoconductor is arsenic selenide.

6. A xerographic plate according to claim 3 wherein said red sensitive photoconductor is gallium triselenide.

7. A xerographic plate according to claim 3 wherein said red sensitive photoconductor is antimony trisulfide.

8. A xerographic plate according to claim 3 wherein said red sensitive photoconductor is mercuric sulfide.

References Cited in the file of this patent

UNITED STATES PATENTS

2,687,484	Weimer	Aug. 24, 1954
2,803,541	Paris	Aug. 20, 1957
2,803,542	Ullrich	Aug. 20, 1957

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,962,376

November 29, 1960

Roland M. Schaffert

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 42, for "of", second occurrence, read -- if --; line 69, for "not" read -- no --; column 4, line 12, for "12B" read -- 12A --.

Signed and sealed this 26th day of September 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD

Commissioner of Patents

USCOMM-DC