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2,803,541

XEROGRAPHIC PLATE

Bernard Paris, Columbus, Ohio, assignor, by mesne assignments, to The Haloid Company, Rochester, N. Y., a corporation of New York

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This invention relates in general to xerography and in particular to a new photoconductive member for xerography.

In Carlson Patent U. S. 2,297,691, there is disclosed a new process of electrophotography which has since become known under the name xerography. According to this process a sensitive member comprising a photoconductive insulating coating on a conductive backing member is sensitized by deposition of an electrostatic charge on the photoconductive insulating layer. The thus sensitized member is then utilized in an electrical photographic process by exposing the member to an optical image, thereby causing selective dissipation of the charge where the light portions of the optical image strike the plate, followed by developing of the residual electrostatic image by treatment with an electroscopic material. The present invention has as its scope and purpose the provision of a new sensitive member particularly suited for and adapted to xerography.

Now, in accordance with the present invention, there is provided a new xerographic sensitive member comprising a conductive backing member having a dual photoconductive insulating layer on at least one surface thereof, the dual layer comprising a carrier layer having on its upper surface a thin photoconductive layer which is a selenium-containing layer. According to one embodiment of the invention, the new xerographic sensitive member comprises a conductive backing material such as, for example, a metal or the like having on its surface a photoconductive layer comprising a carrier layer of vitreous selenium or other material having a thin layer thereon of a mixture of selenium and tellurium. In contrast to comparable selenium members, this new sensitive member is characterized by an increased sensitivity to light as evidenced by a greatly increased conductivity upon illumination, and as evidenced by a change in spectral sensitivity specifically characterized by a substantially increased red sensitivity.

The new xerographic member comprises a base material such as a base plate or other backing member of an electrically conductive material such as a metal or the like. On at least one surface of this member is a carrier layer having a thin layer thereover in the form of a second, photoconductive layer.

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, iron, steel, chromium or the like, or may be of other electrically conductive material such as electrically conductive glass, metallized paper or plastic, or the like, or electrically conductive resins, plastics or like materials. According to a presently preferred embodiment

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of the invention, the backing member consists of an aluminum plate or cylinder having a thin coating thereover of an aluminum oxide layer.

Coated on at least one surface of the base member is the carrier layer comprising, for example, selenium in its vitreous form, sulfur, anthracene, or other insulator-like material characterized by having long ranges for positive hole conduction.

Disposed on the upper surface of the carrier layer is a thin photoconductive layer comprising a thin layer of mixed selenium and tellurium in vitreous form. The top layer comprises generally a layer having a thickness usually in the order of about 2 to 10 microns of selenium and tellurium in which the tellurium content is in the order of about 2 to 45% by weight and preferably between about 5 and about 28%. It will be understood generally that thinner layers of selenium-tellurium mixture will be employed with higher concentrations of selenium.

The combined xerographic member according to the present invention is particularly adapted to operation in xerography wherein the member is sensitized by deposition thereon of a positive polarity electrostatic charge which is subsequently to be selectively dissipated by exposure to an optical image. Under these conditions, the selenium-tellurium layer operates as a photoconductive layer which produces positive holes on exposure to illumination, which positive holes are transmitted through the carrier layer and are neutralized by electrons at the conductive backing surface.

The new sensitive member is hereinafter described in connection with the combination of the selenium-tellurium photoconductive layer disposed over a vitreous selenium carrier layer, although it is to be understood that other carrier layers within the scope hereinbefore set forth may be substituted for the selenium layer.

It has been previously proposed that the xerographic sensitive members may comprise a conductive backing support having thereon a photoconductive layer of the vitreous form of selenium. Such a xerographic plate is characterized by many desirable properties, such as, generally, relatively low dark-decay rate, relatively low residual potentials, and comparatively complete absence of what is known as fatigue. This means, respectively, that: (1) such prior members are capable of accepting and retaining an electrostatic charge on their surface without substantial dissipation in the absence of illumination, (2) in the presence of illumination, the potential difference across the xerographic plate will diminish to a low value, and (3) such prior members are characterized by comparatively good retention of these properties throughout successive cycles of the xerographic process. A theory propounded to explain these and other properties of xerographic plates is that vitreous selenium in the absence of light has a very low density of free current carriers, and that carriers such as positive holes freed by the action of light are able to migrate substantially through the vitreous selenium layer without being trapped. It is, therefore, apparent that a vitreous selenium layer is ideally characterized by operating as a good transporter of positive holes. In contradistinction to a vitreous selenium layer, it is presently understood that a layer comprising a mixture of selenium and tellurium is characterized by shorter free paths for positive holes and is characterized by a greater density of free current carriers in the absence of light. The photoconductive characteristics of mixtures of selenium and tellurium, however, are much superior to those of vitreous selenium. In particular, mixtures of selenium and tellurium respond photoconductively to all visible radiations, whereas vitreous selenium responds only to blue and green radiations of the visible spectrum. Moreover, the sensitivity to blue and

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green light is greater with mixtures of selenium and tellurium than with vitreous selenium.

According to the present invention, the beneficial properties of the vitreous selenium layer as a material with a small density of free carriers in the absence of light and as a material which is a good transporter of photon-liberated positive holes are utilized in combination with the excellent photo-conductive properties of a selenium-tellurium mixture to yield the improved xerographic member.

According to one method of preparation, an aluminum plate is placed under high vacuum in the order of less than about 1 micron of mercury pressure and a layer of vitreous selenium is evaporated thereon while maintaining the aluminum plate at a temperature between about 60° and about 90° C., and preferably in the order of about 75° C. The deposition of the selenium layer is halted when the layer has reached the desired thickness such as, for example, in the order of about 10 to 200 microns. A second layer then is evaporated onto the surface from an evaporation source consisting of a mixture of selenium and tellurium containing tellurium in substantially the percentage desired in the photoconductive generating layer. The photoconductive layer of selenium and tellurium desirably is thinner than the vitreous selenium carrier layer and may be as small as 0.03 micron or as large as 50% of the thickness of the carrier layer, but usually not less than 0.1 micron, nor more than 20% of the thickness of the carrier layer. Thus, for example, there may be prepared a sensitive member comprising a backing plate, a vitreous selenium layer in the order of about 20 microns, and a selenium-tellurium overcoating in the order of about 1 micron thickness. This new member is characterized by relatively low dark decay and absence of fatigue in combination with increased photoconductive speed and substantially improved sensitivity to red, yellow, and green lights.

Other methods of preparation of new xerographic members, according to this invention, may be employed, but vacuum evaporation is the presently preferred method and the following examples are presented in illustration of simple and straightforward methods of achieving the advantages of this new improvement in the art. The new improved xerographic members can be prepared by pressing molten layers onto a base member or by spraying molten composition or pigmented binder films onto such base members, but it is to be realized that the production of high quality members, such as are desired for photographic purposes, is most satisfactorily achieved by procedures including vacuum evaporation.

Example 1.—A brass plate having a smooth, flat surface approximately 4" x 5" was thoroughly cleaned by scrubbing in water containing a detergent. The plate was rinsed clean and was then polished with a cleaning material believed to have a hydrocarbon wax base and being available under the trade name "Glass Wax." This polish was applied uniformly over the surface of the plate and was 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 was placed in an evacuation chamber in contact with a platen through which is circulated water at a controlled temperature. The chamber was evacuated and the water temperature set to control the temperature of the brass plate at 80° C. Selenium placed in molybdenum evaporation boats was then brought to a position about 6" from the surface of the plate, and the selenium was evaporated onto the surface by heating from electrical heaters located at the molybdenum evaporation boats. A layer of selenium about 15 microns thick was deposited on the brass plate. Next, and without destroying the vacuum condition, other molybdenum boats containing a mixture of 7% tellurium in selenium were heated to evaporate onto the surface of the selenium coated plate a film approximately 5 microns

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thick of mixed selenium-tellurium. After the evaporation was complete, the plates were removed from the vacuum chamber and found to be photoconductive insulating members suitable for xerography. As tested against comparable plates having 20-micron layers of selenium with no tellurium mixed therewith, the new plates were found to have greater light sensitivity, particularly to green and yellow light. Xerographic pictures of good quality were produced from these new xerographic members.

Example 2.—The procedure of Example 1 was repeated employing percentages of tellurium in the upper selenium-tellurium layer of 2%, 4%, 7%, and 8% and employing films of 5 microns of selenium-tellurium mixture deposited on top of films of 15 microns of selenium to yield films of total thickness of 20 microns. The thus produced plates were characterized by increased xerographic sensitivity particularly to green and yellow light with the plates having layers containing 7 and 8% selenium exhibiting the greater increase in sensitivity. Xerographic prints of such quality were produced on all of these plates.

Example 3.—The procedure of Example 1 was repeated at plate temperatures during evaporation of 60°, 70°, 80°, and 85°. Plates of comparable quality were produced at all these evaporation temperatures.

Example 4.—The procedure of Example 1 was repeated to produce plates having total selenium and selenium-tellurium layers in thickness of 60 microns of which the selenium-tellurium layer comprised 10% or 6 microns placed on top of the all-selenium layer. A series of plates was prepared at a plate temperature during evaporation of 80° C. and an evaporation time of 10 minutes for the selenium layer and 60 minutes for the top selenium-tellurium layer. Within this series of plate preparation, the tellurium content in the selenium-tellurium layer was set for the different plates at 0, 7, 8, 10, 12.5, 17.5, 15, and 20% tellurium, the remainder being selenium.

In testing the plates according to this example, two tests are recorded. According to the first test, the plate is charged to about 600 volts and in the absence of illumination the dissipation of this potential was measured with respect to time. The dark decay half-time, which is the time required for this potential to decrease to ½ its original value, was recorded for each of the plates and was found to be 630 seconds for the plate having a layer containing 7% tellurium and 12 seconds for the plate having a layer containing 20% tellurium, with the intermediate percentages of selenium resulting in correspondingly intermediate dark decay half-times. The plate containing no tellurium in the upper layer had a dark decay half-time greater than 1000 seconds.

The second test recorded the sensitivity of the plate in terms of reciprocal seconds for the plate potential to drop from 200 to 100 volts when exposed to 0.030 microwatt per square centimeter radiation. This test was performed at different wave lengths of radiation to measure spectral sensitivity as well as total sensitivity. The plate having an upper layer containing 20% tellurium showed a peak sensitivity of about 1.4 reciprocal seconds at about 500 millimicrons wave length with the sensitivity being greater than 1.0 over the range from less than 400 millimicrons to over 600 millimicrons wave length. Significant sensitivity was measured through the entire visible spectral range. The plate having no tellurium in its upper layer showed a peak sensitivity of about 0.3 reciprocal seconds at a wave length of about 400 millimicrons and showed almost no sensitivity above 550 millimicrons wave length. In the intermediate values, intermediate sensitivities were noted. For example, the plate containing 10% tellurium in its upper layer showed a peak sensitivity of about 0.7 reciprocal seconds at about 400 millimicrons wave length and showed significant sensitivity throughout the spectral range up to greater than 650 millimicrons wave length.

Example 5.—A series of xerographic plates was prepared with a total selenium and selenium-tellurium thicknesses of 50 microns, of which 2% or 1 micron was the selenium-tellurium layer on top of the base selenium layer. These plates were prepared at 80° backing-plate temperature during evaporation and contained 25% tellurium in the selenium-tellurium layer. A number of such plates was prepared and tested for the production of xerographic pictures; uniformly good xerographic results were achieved. The plates were characterized by substantially increased sensitivity throughout the visible spectral range. These plates averaged 12 times the speed of comparable selenium plates having no selenium-tellurium layer.

A xerographic member, such as the one just described, is particularly adapted to xerography employing positive polarity charging to a potential in the order of about 50 to about 500 volts followed by exposure to an optical image whereby there is selective dissipation of the electrostatic charge. The resulting electrostatic latent image can be developed by treatment with an electroscopic material, and optionally the developed image is transferred to a transfer member to yield a xerographic print.

It is to be understood that other methods of preparation of the xerographic member may be employed including, for example, melting and pressing or spraying molten selenium onto a base member or, if desired, painting or spraying the surface of the base member with a pigmented resin where pigment is selenium in its vitreous form or other photoconductive material of the type hereinbefore described as the photoconductive carrier. Likewise, the selenium-tellurium layer may be formed by simultaneous evaporation from separate sources for the selenium and tellurium as well as by evaporation of a mixture of selenium-tellurium or may be applied by other methods such as spraying a molten mixture or melting and pressing a mixture of the ingredients onto the base member having the photoconductive carrier layer thereon.

The operability and operation of the new xerographic member has been described in terms of theory of solid state physics and thus in terms of migration of electron and positive holes within solid state structure. It is to be understood, however, that the operation of the invention is not limited to the correctness of the theory and that the present invention, therefore, is not to be limited to this or any other particular mechanism of operability.

What is claimed is:

1. An improved photoelectrically sensitive member comprising a conductive backing member having thereon a carrier layer consisting of vitreous selenium and a

thin layer thereover consisting of a mixture of selenium and tellurium in their vitreous form.

2. The article according to claim 1 wherein the selenium-tellurium layer consists of between about 2 and about 45% tellurium and substantially the remainder selenium.

3. The article of claim 1 wherein the selenium-tellurium layer consists of about 5 to about 28% tellurium and the remainder substantially selenium.

4. A photoelectrically sensitive member comprising a conductive backing member having thereon a carrier layer consisting of vitreous selenium and a thin layer thereover of a mixture of selenium and tellurium in their vitreous form, said thin selenium-tellurium layer consisting of between about 2 and about 45% tellurium, the balance being substantially selenium, and being at least about 0.03 micron thick but not more than about 50% as thick as the carrier layer.

5. An article according to claim 4 wherein the thin selenium-tellurium layer consists of between about 5 and about 28% tellurium, the balance being substantially selenium.

6. An article according to claim 5 wherein the thin selenium-tellurium layer is at least about 0.1 micron thick but not more than about 20% as thick as the photoconductive carrier layer.

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