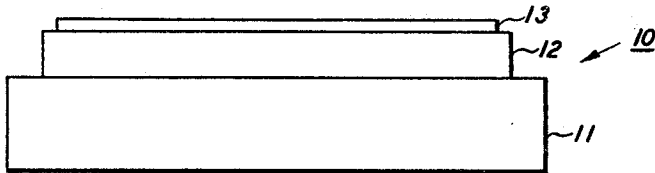


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LIGHT INSENSITIVE XEROGRAPHIC PLATE  
AND METHOD FOR MAKING SAME  
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**LIGHT INSENSITIVE XEROGRAPHIC PLATE AND METHOD FOR MAKING SAME**

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**ABSTRACT OF THE DISCLOSURE**

A light insensitive xeroradiographic plate comprising a conventional photoconductive insulating layer overlying an electrically conductive support member, and a thin layer consisting of light insensitive selenium overlaying said photoconductive insulating layer.

This invention relates in general to xerography and, more specifically, to an improved xeroradiographic plate.

In the art of xerographic copying, as originally disclosed by Carlson in U.S. Patent 2,297,691, and as further described by many related patents in the field, xerographic plate containing a photoconductive insulating layer is first given a uniform electrostatic charge in order to sensitize its entire surface. The plate is then exposed to an image of activating electromagnetic radiation such as light, X-ray, or the like which selectively dissipates the charge in the illuminated areas of the photoconductive insulator while leaving behind a latent electrostatic image in the non-illuminated areas. This latent electrostatic image is then developed and made visible by depositing finely divided, electroscopic marking material on the surface of the photoconductive insulating layer. Where reusable photoconductive insulating material is used, the visible image formed by the electroscopic marking material is transferred to a second surface, such as a sheet of paper, and fixed in place thereon to form a permanent visible reproduction of the original image. Where a non-reusable photoconductive insulating material is used, the marking material or toner particles are directly fixed in place on the surface of the non-reusable insulating material thereby eliminating the transfer step from the previous process.

Presently, high quality xerographic plates employing a photoconductive layer of amorphous or vitreous selenium are being used with great success. These plates are illustrated in U.S. Patent 2,970,906 to Bixby. The amorphous selenium plate is responsive to both visible light and the X-ray portion of the electromagnetic spectrum. As a result of this wide spectral range of light sensitivity, the plates must be carefully handled and protected from visible light when they are used for X-ray imaging. It can therefore be seen that selenium plates which are to be used in X-ray xerography, hereinafter referred to as xeroradiography, must be stored and used under dark room conditions. There is, therefore, a need for xeroradiographic plates which are insensitive to visible light while still being responsive to X-ray radiation. Such a plate having the properties of light insensitivity would permit continuous observation of the X-ray process under normal illumination and thus eliminate the need for additional apparatus required to maintain dark room conditions.

It is, therefore, an object of this invention to provide an improved xeroradiographic plate and an improved method for preparing said plate which overcomes the above noted disadvantages.

It is another object of this invention to provide a xeroradiographic plate which is substantially insensitive to visible light.

It is a further object of this invention to provide a method for preparing a xeroradiographic plate which is substantially insensitive to visible light.

The foregoing objects and others are accomplished in accordance with this invention by preparing a xeroradiographic plate which is made substantially insensitive to light by depositing a thin coating of about 1 to 20 microns of low carrier range selenium or a thin coating of selenium doped with a material having a low carrier range onto "normal" selenium or some other photoconductor such as those disclosed in U.S. Patents 2,803,542; 3,121,006; 3,121,007; and 3,151,982 to Ullrich, Middleton et al., Middleton et al., and Corrsin, respectively. The term "normal" selenium means that most of the carriers are able to move across a charged selenium layer when exposed to activating electromagnetic radiation. Normal selenium will hereinafter be referred to as conventional selenium or simply selenium.

By way of illustration, with no intent to limit the method of preparing a conventional selenium plate, a selenium plate may be prepared in the following manner: A metal support backing plate such as brass or aluminum is cleaned and then positioned in a vacuum chamber with a temperature control means for the backing plate, such as for example, a contacting temperature control platen provided with water cool means. The vacuum chamber is then evacuated to a low pressure, such as about 1 micron of mercury, or less. A layer of high purity (99.99%+) selenium is then evaporated at a temperature of about 280 to 300° C. onto the plate. The selenium may be placed in any inert refractory container such as molybdenum, Pyrex, or the like. Common thicknesses for selenium plates range from 20 to 100 microns. When used for X-ray imaging or other high energy electromagnetic radiation, much thicker layers on the order of 160 to 500 microns may be employed to take advantage of the increased stopping power of the thicker layer when exposed to the high energy penetrating radiation.

The advantages of the improved xeroradiographic plate and the method for producing said plate will become more apparent upon the following disclosure of the invention and when taken in conjunction with the accompanying drawing wherein:

The drawing is a schematic sectional view of one form of xeroradiographic plate according to the invention.

In the drawing reference character 10 designates an embodiment of one xeroradiographic plate according to the invention. This plate has a conventional electrically conductive support member 11 such as brass, aluminum, steel or the like. The support member may be of any convenient thickness, rigid or flexible, and may be in the form of a sheet, web, cylinder or the like. It may also comprise other materials such as metallized paper, plastic sheets covered with a thin coating of aluminum or copper iodide or glass coated with a thin layer of chromium or tin oxide. Reference character 12 designates a conventional photoconductive insulating layer such as amorphous selenium, selenium and arsenic, selenium with photoconductive particles dispersed therein, or a non-photoconductive binder saturated with photoconductive particles. This layer commonly ranges from about 20 to 100 microns for normal xerographic applications and may be as high as 500 microns for X-ray application. Reference character 13 represents a thin outer layer of selenium having a low carrier range or selenium doped with an additive to impart a low carrier range. The thickness of this layer may range from about 1 to 20 microns, and usually ranges up to about 10 percent of the thickness of the selenium substrate 12.

This invention contemplates the use of a thin coating or layer of low carrier range selenium or low carrier range

selenium formed by doping with a halogen or thallium over a conventional selenium layer such as that described above.

When the plate is formed by the application of a thin layer of low carrier range selenium, said layer may be formed by evaporating the thin layer of conventional selenium onto a relatively cold substrate of a conventional selenium plate. Temperatures in the range of 15 to 35° C. have been found to provide a satisfactory substrate for the evaporation of the thin outer layer which exhibits a low carrier range when charged to a positive voltage. If the temperature exceeds about 35° C., the thin selenium layer loses its low carrier range properties and becomes sensitive to light similar to the normal conventional selenium substrate upon which it is coated. A suitable thickness for the outer layer of low range selenium is in the range of 1 to 20 microns. The formation of the thin layer of selenium on the conventional selenium plate under these conditions results in a thin layer of low range selenium on a thicker base layer of conventional selenium. When charged positive, the surface of this plate is insensitive to light and when exposed to X-ray radiation, it creates carriers throughout the bulk of the conventional selenium layer, with the carriers so created, moving easily to the surface and thus discharging the plate. The areas unexposed to X-ray radiation remain charged, and the latent electrostatic image can be developed in the normal xerographic manner.

When the light insensitive plate is formed by doping with a thin layer of thallium, a pre-alloy mixture of thallium and high purity selenium is placed in a molybdenum boat in a vacuum chamber and vacuum evaporated onto a normal selenium plate such as has already been described. The thickness of the thallium mixture may be of any convenient thickness such as from 1 to 20 microns. The concentration of the thallium ranges anywhere from a few parts per million to 10,000 parts per million. Although the concentration of thallium may range widely, it is usually convenient to maintain the concentration from 10 to 1,000 parts per million with the amount of thallium used being only that necessary to render the plate insensitive to light. When using the thallium doped layer, it is necessary to charge the plate positive in order to render it insensitive to light.

When a halogen is used as the dopant to form the low carrier range layer, the concentration of the halogen may be controlled by mixing the desired concentration from master alloys which may be made in the laboratory by standard techniques. Concentrations from the few parts per million up to 10,000 parts per million are effective with the amount of dopant used being only that necessary to render the plate insensitive to light. Ranges of 10 to 1,000 parts per million are normally suitable to render the plate insensitive to light. The total thickness of the outer coating is conveniently from 1 to 20 microns. To render the halogen coated plates insensitive to light, it is necessary that they be negatively charged at their surface.

The thickness of the low carrier range selenium layer, formed either by evaporating on a cold substrate or by doping with a suitable material, need only be as thick as that necessary to render the plate insensitive to light. Thicknesses of from 1 to 20 microns have proven satisfactory, but this range is not intended to be limiting as layers outside this range are also effective. In the doped low carrier range selenium layers, the concentration of the thallium and the halogen need only be present in amounts necessary to render the layer insensitive to visible light while still being sensitive to high energy penetrating radiation, outside the visible spectral range. If, for example, under given conditions, 1,000 parts per million are effective to render a plate insensitive to light then it would be unnecessary and uneconomical to use 10,000 parts per million. When the low range layer is formed on a cold substrate, the layer thus formed exhibits low range carrier properties at forming temperatures below about 35° C.

Any convenient temperature below 35° C. appears to be satisfactory, with 10 to 35° C. being preferred, in that temperature above about 35° C. result in the evaporated layer being light sensitive, while temperatures below about 10° C. require special apparatus to insure that the cold substrate is accurately maintained at the proper temperature.

The following examples further specifically define the present invention with respect to the method of making double layered xeroradiographic plates which are insensitive to visible light. The parts and percentages in the disclosure are by weight unless otherwise indicated. The examples below are intended to illustrate various preferred embodiments of this invention.

#### EXAMPLE I

A conventional selenium plate is made by placing a brass backing plate on a water cooled support member within a vacuum chamber. A source of high purity selenium is placed in a Pyrex boat below the brass plate. The chamber is then evacuated to a pressure of about 0.5 micron of mercury. The Pyrex boat is heated to a temperature of about 280° C. to evaporate a uniform amorphous coating of selenium to a thickness of about 100 microns onto the brass plate. During the evaporation step the brass plate is maintained at a temperature of about 60° C. After completion of the evaporation step, the thus formed plate is charged positively with a corona discharge electrode to a voltage of about 600 volts. The entire plate is then exposed to light. The previously charged surface is substantially discharged by the light exposure, rendering the plate substantially insensitive to X-ray radiation. The plate is again charged to a voltage of 600 volts and kept under dark room conditions. While unexposed to light the plate is subjected to a pattern of activating X-ray radiation whereby the electrostatic surface charge is dissipated in the areas energized by the X-ray radiation, while the areas unexposed to the radiation remain unaffected, forming a latent electrostatic image which is developed in any conventional xerographic manner.

#### EXAMPLE II

A plate having a 100 micron layer of selenium is made in the conventional manner already described above in Example I. This plate is then placed in a vacuum chamber on a water cooled support platen. A source of high purity selenium is then placed in a molybdenum boat in the vacuum chamber below the selenium plate. The chamber is then evacuated to a pressure of about 0.5 micron of mercury and the molybdenum boat maintained at a temperature of about 280° C. to evaporate a 5 micron coating of selenium onto the selenium plate which is maintained at a temperature of about 15° C. After the completion of the evaporation step and cooling, the vacuum is broken and the plate is removed from the vacuum chamber. The double layered selenium plate is then charged to a positive polarity with a corona discharge electrode, as described in U.S. Patent 2,777,957 to Walk-up, to a voltage of about 600 volts. The resulting plate is substantially insensitive to visible light. This plate is then exposed to X-ray activating radiation whereby the electrostatic charge on the surface is dissipated in the areas energized by the X-ray radiation while the areas unexposed to the X-rays remain unaffected, forming a latent electrostatic image which can be developed in the normal xerographic manner.

#### EXAMPLE III

A plate having a layer of selenium 160 microns thick contained on aluminum is made in the conventional manner described in Example I. A master alloy of high purity selenium containing 1,000 parts per million of thallium is placed in an inert Pyrex evaporation boat in the vacuum chamber. The vacuum chamber is then sealed and evacuated to a pressure of approximately 0.5 micron of mercury while the aluminum plate is held at a temperature of

about 70° C. The Pyrex boat is heated to a temperature of about 280° C. to evaporate a 4 micron coating of the selenium-thallium mixture onto the selenium plate. After completion of the evaporation step the vacuum is broken and the chamber cooled to room temperature. The double layer plate is moved from the evacuation chamber and charged positively to about 700 volts with a corona discharge electrode as described in Example II. This plate is insensitive to visible light and readily responds to penetrating radiation of the X-ray type as the plate described in Example II.

#### EXAMPLE IV

A 120 micron layer of selenium on brass is made in the manner described in Example I. A master alloy of 500 parts per million chlorine in high purity selenium is placed in an inert Pyrex evaporation boat in an evacuation chamber as described in Example II. The selenium chlorine mixture is evaporated to a thickness of 3 microns onto the selenium plate under conditions similar to that set forth in Example III. The resulting double layer plate is then charged negative to a voltage of 600 volts as described in Example II above. This plate is insensitive to visible light, but responds well when exposed to X-ray radiation.

#### EXAMPLE V

A selenium layer 200 microns thick on brass is made in the manner described in Example I. A master alloy of 500 parts per million of bromine in high purity selenium is placed in an inert Pyrex evaporation boat in an evacuation chamber and evaporated to a thickness of 4 microns onto the conventional selenium plate under the conditions described in Example III. The resulting plate is insensitive to visible light and responds well when exposed to X-ray radiation.

#### EXAMPLE VI

A 150 micron plate of conventional selenium on aluminum is made in the manner described in Example I. A master alloy of 1,000 parts per million of iodine and high purity selenium is placed in an inert Pyrex evaporation boat in an evacuation chamber as described in Example III. The selenium-iodine mixture is evaporated to a thickness of 5 microns onto the conventional selenium plate under the conditions set forth in Example III. This plate is insensitive to visible light and readily responds to penetrating radiation of the X-ray type as the plates described in Examples II-V.

The plates made in accordance with the present invention are normally used in a xeroradiographic process which includes at least the three basic steps of charging, exposing, and developing. If the plate is coated with low range selenium evaporated at less than about 35° C. or is doped with thallium, the plate must be charged to a positive polarity in order to render its insensitive to light. On the other hand, if the low carrier range outer coating is doped with a halogen, the plate must be charged to a negative polarity in order to render it light insensitive. The plates are then exposed to X-ray radiation which se-

lectively dissipates the previously applied charge. Through the use of these plates, as set forth above, the need for dark room conditions is entirely eliminated.

Although specific components, proportions, and procedures have been stated in the above description of the preferred embodiments of the invention, other suitable materials such as those listed above, may be used with similar results. In addition, other materials and procedures may be varied to synergize, enhance, or otherwise modify the end result. For example, during the evaporation step in the manufacturing of the conventional selenium plate, the low carrier range outer coating may be evaporated onto the freshly made conventional selenium plate immediately upon the termination of the evaporation of the conventional selenium layer. Also, the alloy mixtures for the low carrier range coatings, may be made from commercially available master alloys or prepared in the laboratory by conventional means such as simply mixing the appropriate amount of additive element with the high purity selenium.

What is claimed is:

1. A light insensitive xeroradiographic plate comprising a conventional photoconductive insulating layer overlaying an electrically conductive support member, and a thin layer consisting essentially of light insensitive selenium overlaying said photoconductive insulating layer, said light insensitive selenium being selected from the group of thallium doped selenium and halogen doped selenium.

2. The plate of claim 1 in which the light insensitive selenium layer is doped with a halogen in a concentration from about 10 to 10,000 parts per million.

3. The plate of claim 2 in which the thickness of the light insensitive selenium layer is from about 1 to 20 microns.

4. The plate of claim 1 in which the light insensitive selenium layer is doped with a thallium in a concentration from about 10 to 10,000 parts per million.

5. The plate of claim 4 in which the thickness of the thallium doped layer is from about 1 to 20 microns.

6. A method of preparing a light insensitive xeroradiographic plate which comprises the steps of evaporating a thin layer of thallium doped selenium onto the surfaces of a conventional photoconductive layer wherein the thallium is present in a concentration from about 10 to 10,000 parts per million.

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