This invention relates in general to the art of xerography, and in particular to an improved xerographic plate for use in the xerographic process. More specifically, the invention relates to an improved xerographic plate comprising a conductive backing having on at least one surface thereof a charge carrier layer of specially treated vitreous selenium on which there is a thin photoconductive overlayer consisting of an alloy of selenium-tellurium, and to an improved method of xerography therewith.

In the art of xerography, as disclosed in Carlson U.S. Patent 2,297,691, it is usual to form an electrostatic latent image on a xerographic plate which comprises a conductive backing member such, for example, a metallic surface having a photoconductive insulating layer 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 an image pattern of activating radiation, and, in general, is highly sensitive to light primarily in the blue, green spectral range.

From this description of the basic process of xerography, it is evident that the unique properties of the photoconductive insulating layer are critical for the successful operation of the process. This layer must have a resistivity of at least about 10^{12} ohms-cm, in the dark in order to retain an electrostatic charge on the surface for a significant period of time and desirably it has a resistivity even greater than this. It must also have the property of lowering its resistivity on activation by radiation. The discovery of the photoconductive insulating property of highly purified vitreous selenium has resulted in this material becoming the standard in commercial xerography. It has outstanding light sensitivity, and is also outstanding in its dark resistivity which is at least about 10^{12} ohms-cm.

Since selenium was first employed as a xerographic plate conductor, much progress has been made in the understanding of solid state physics theories and mechanisms applicable to such use. Briefly, it has been found that vitreous selenium conducts both electrons and holes and that the mobility for holes is approximately ten times that for electrons. Thus, vitreous selenium, while possessing a long range for holes, has a very short range for electrons. So strongly does amorphous selenium trap electrons that Weimer in U.S. Patent 2,687,484 states that the material has "little or no electron conductivity." Accordingly, it has become the standard in xerography to use vitreous selenium layers with positive polarity sensitizing charges thereon.

Advances in the art have disclosed xerographic plates with increased spectral sensitivity particularly toward the red end of the spectrum as well as generally increased sensitivity or speed. As disclosed in Ulrich, U.S. Patent 2,803,541, improved plate properties are obtained utilizing a mixture of arsenic and selenium. In Mengali U.S. Patent 2,745,327, there is disclosed improved plate properties utilizing a photoconductor comprising a mixture of selenium with tellurium, whereas in Paris U.S. Patent 2,803,541, a mixture of selenium and tellurium is utilized in a thin layer overcoating the photoconductor of predominantly vitreous selenium. Each of these known structures when incorporated into a xerographic plate enhances the photoconductive properties in what is regarded as a highly desirable area, i.e., increased speed and spectrality.

However, despite these advantages, xerographic plates other than essentially pure vitreous selenium have not enjoyed commercial success. One reason for their lack of commercial success has been the inability heretofore to reproduce these plates reliably with consistency of characteristics within tolerable ranges. In addition, these plates under other than laboratory conditions, i.e., under continuous use and recycling experienced in the xerographic process, experience relatively high dark decay, relatively high residual potential, and high orders of fatigue as compared to photoconductive layers of commercially available vitreous selenium. By this, it is meant that these alloyed plates of the types referred to generally suffer from an increased impairment of desirable operating properties in successive cycles of the xerographic process. In the early period of xerography it was common to employ manual processing procedures in connection with a set of individual xerographic plates. Under these conditions each plate was reused relatively infrequently. Now, however, xerography is increasingly concerned with automatic processing equipment employing a single continuously rotating cylindrical xerographic plate. In such machines each portion of the sensitive surface of the plate may be repetitively recycled as many as about 10 times per minute. Thus, the recycling requirements for xerographic plates have become very severe. Furthermore, as stated above, these plates of the prior art, including any pure vitreous selenium, have been limited to utilization with initial sensitizing charges of positive polarity because of their long range for holes while having a short range for electrons such that they are unsuitable for sensitizing with charges of negative polarity.

Now in accordance with the present invention there is provided an improved xerographic plate of specially processed selenium with an overlying selenium-tellurium alloy layer, having increased speed with increased spectral sensitivity and good reproducibility and adapted for repetitive cycling. There is also provided an improved method of using such a plate in repetitive cycles whereby the plate is negatively charged before exposure and positively charged before reuse. The advantages to xerography of such a plate are many, offering opportunity for increased utility by increased spectral response while permitting more flexibility and more efficient and rapid performance of the xerographic process.

It is therefore an object of the invention to provide improved xerographic plates having increased speed and sensitivity and adapted for cyclic reuse.

It is a further object of the invention to provide a xerographic plate with increased spectral sensitivity that can be utilized with sensitizing charges of negative polarity.

It is a further objective of the present invention to provide a xerographic plate having a layer of specially processed selenium and a thin layer of selenium-tellurium alloy coated thereon.

It is a further objective of the invention to provide an improved method of operating xerographic plates in repetitive cycles.

These and other objects are attained in accordance with the invention utilizing a xerographic plate comprising a conductive backing member having thereon a charge storage layer of vitreous selenium that has been processed in a manner to be described, and an upper thin photoconductive layer containing a selenium-tellurium alloy as hereinafter described. The plate when being utilized in
the xerographic process in which it is successively and repetitively subjected to charging, exposing, and developing, has been found to be particularly superior when employed in a manner to be described. More specifically, when employed in this manner, a plate is repetitively cycled in a process including negative charging, exposure to an image pattern of radiation, development, transfer, cleaning, and positive charging with concomitant uniform illumination.

In the drawings:

FIG. 1 isometrically illustrates a xerographic plate in accordance with the invention;

FIG. 2 schematically illustrates in section an apparatus arrangement in accordance with the invention; and

Figs. 3, 4, and 5 are graphs which illustrate characteristic properties of a xerographic plate in accordance with the invention compared to characteristics of a plate of the known art.

Referring to FIG. 1 there is illustrated a xerographic plate 10 comprising a conductive backing member 11 on which there is supported a charge storage layer 12 which in accordance with the invention is specially processed amorphous selenium, and on top of which is a thin photoconductive layer 13 of a selenium-tellurium alloy. Because of the thinness of layer 13 and in order to protect it from wear, a thin but durable and transparent insulating overcoating 14 of a type to be described is preferably optionally applied over layer 13 solely for mechanical protection.

Referring to FIG. 2, the plate 10 is shown cylindrical in form and adapted to be continuously rotated by a motor M-1 in the direction indicated by the arrow. As the drum rotates, an electrostatic charge is applied to its surface by a corona generating device 20 which may be of a type disclosed in Vyverberg U.S. Patent 2,836,725 and connected to a source of high potential 21. The charge applied by generator 20 is positive in polarity and on the first cycle of operation is termed "pregeneration" whereas thereafter for subsequent cycles is termed "re-generation," as will be understood by the description to follow. The region of the plate being charged by generator 20 is concomitantly exposed by a source of activating radiation such as illumination source 22, that suitable lamp may be an incandescent lamp, fluorescent lamp or the like. A light shield 19 prevents light from reaching the drum past the immediate vicinity of the lamp.

Next in the direction of rotation, the drum surface passes a corona generator 23, similar to generator 20 mentioned above, which applies a sensitizing potential of negative polarity on the drum surface usually on the order of −300 volts to −1000 volts. After charging, the surface is exposed to a light image of copy 24 being advanced from a supply reel 25 to a takeup reel 26 at a rate proportional to the rate of drum rotation. As the copy advances past the optical axis of objective lens 27, it is illuminated by lamps 28 and projected by the lens through an exposure slit 29 incrementally onto the drum surface. This selectively causes dissipation of the image charging potential to form an electrostatic latent image in image configuration of the original copy.

The electrostatic latent image is developed by a developing apparatus 40 that may be of a suitable type known to those in the xerographic art as for example disclosed in U.S. Patent 2,945,434 and which may utilize a powdered resin that is cascaded over the drum surface and is electrostatically attracted to the electrostatic latent image to render it visible. The developed image may then be transferred to a secondary support surface 41, which may be paper or the like, drawn from a supply reel 42 onto a takeup reel 43 being driven also from motor M-1.

The support surface contacts the drum in the vicinity of corona generating device 44, which is similar to corona generating devices 20 and 23 mentioned above, and which applies an electrostatic charge of appropriate polarity to the back of the paper for effectively transferring the developed image from the drum to the paper. Thereafter the support surface passes through a suitable fusing apparatus 45 which may be a heat fuser of the type disclosed in Crumrine U.S. Patent 2,852,651 or a vapor fuser of a type disclosed in Carlson U.S. Patent 2,747,637 wherein the loosely supported developed image on the support surface is permanently affixed thereto. The drum continues to pass to a cleaning station at which a brush 46 or the like cleans the drum in preparation for recycling. Subsequently the plate passes by generator 20 which applies opposite polarity to that applied by 23, but preferably of substantially similar order of magnitude.

The general nature of the invention having been set forth for illustrative purposes only, the following examples are now presented as illustrations but not limitations of the methods and means for carrying out the invention. In the following examples, the plates were prepared on an aluminum substrate by vacuum evaporation of the photoconductive materials while the base was held at 60° C., in each case the substrate having first been processed by heating in a solution of 3% sodium carbonate and 3% tri-sodium phosphate at 65° C. for 45 seconds after which it was rinsed twice in distilled water and then heat treated and allowed to dry at 200° C. for 105 minutes.

**Example 1**

A 40 micron charge storage layer of specially processed amorphous selenium was vacuum evaporated as a base onto the aluminum substrate and a 0.1 micron layer of selenium-tellurium alloy was evaporated thereover without breaking the vacuum. Processing of the selenium included placing substantially pure selenium in a glass ampule with an amount of titanium wire equal to approximately 7½ percent of the weight of selenium and placed at one end of the ampule. The ampule was evacuated to 20 to 30 microns of mercury pressure, sealed, and then heated in an oven at approximately 522° F. for two hours after the selenium had melted, with constant contact between the molten selenium and the titanium wire. At the end of the treatment, the ampule was tipped so that the molten selenium drained away from the wire and then cooled. The ampule was broken and the selenium broken up and placed in the evaporating crucible. A selenium-tellurium alloy comprising approximately 25% by weight of tellurium was prepared by heating the materials together for approximately two hours in a vacuum sealed glass tube 450° C., cooling, and pulverizing. After evaporation of the selenium, small increments of the pulverized alloy were dropped into a separate crucible, heated to 500° C. until the 0.1 micron alloy layer was obtained. The resulting xerographic plate was then coated with the vacuum and dipped in a solvent solution of nitrocellulose to provide an abrasion resistant protective layer approximately 2 microns in thickness.

**Example 2**

A glass tube containing 50 grams of selenium and 20 grams of analytical reagent iron wire of a type marketed by the Mallinckrodt Chemical Company was evacuated, sealed and heated to 350° C. for 24 hours after which the contents were vacuum evaporated onto an aluminum substrate to form a 40 micron layer of vitreous selenium. A mixture of 25 parts tellurium and 75 parts selenium by weight was processed identically as in Example 1 to form an alloy and was also vacuum evaporated onto the vitreous selenium layer. A transparent protective overcoating of nitrocellulose approximately 2 microns thick was then applied over the tellurium-selenium layer similarly as in Example 1.

**Example 3**

A plate was prepared similarly as in Example 2 except that the selenium used for the layer of vitreous selenium was processed in a glass tube with the same weight of selenium but with 50 grams of analytical reagent iron wire.
Selenium layers which are specially processed in accordance with the procedures illustratively illustrated in Examples 1, 2, and 3 are characterized as having a low dark discharge rate when negatively charged and a high range and mobility for negative charge carriers as demonstrated by substantial light sensitivity when negatively charged, although light sensitivity is not employed in the present invention. Each plate thus prepared was then subjected to a series of tests to determine various characteristic properties of spectral sensitivity, spectral response and electrical contrast, each to be described. The test for spectral sensitivity consisted of exposing through a slit to the previously sensitized plate from an enlarger with a No. 2 Photoflood incandescent lamp and interference filters at 400, 500, 600, and 680 millimicron wavelength. The plates were sensitized with charge of negative polarity. Light intensity was measured with a calibrated Densichron and the plates were tested after numerous repetitive cycles of charging and exposure and termed to be in “a well-cycled condition.” A commercial selenium plate obtained from Xerox Corporation, of Rochester, New York, was used as a standard comparison test plate. To obtain the best results with this plate, it was sensitized with positive polarity as recommended by the manufacturer. The spectral sensitivity of plates of the examples were found to be substantially similar to each other, although the plate of Example 3 showed slight superiority having slightly increased spectral sensitivity over the plates of Examples 1 and 2.

Referring to FIG. 3, the spectral sensitivities of the various plates are graphically illustrated in terms of “quantum efficiency” plotted as the ordinate against wavelength as the abscissa. By “quantum efficiency” is meant that plate property consisting of the measured flow of charge in excess of dark current per photon of light energy incident on the plate and expressed as a percentage. Curve A represents the test plate (i.e., the commercial selenium plate) while curve B represents the plate of Example 1 and curve C represents the average of the plates of Examples 2 and 3. From these curves it may be seen that plates constructed in accordance with the invention and represented by curves B and C have increased spectral response, the sensitivity extending to 700 millimicron wavelength, as compared to the selenium plate of the prior art which is generally not sensitive beyond 600 millimicrons, while at the same time the plates of the invention have a greater quantum efficiency, or in other words a generally increased sensitivity to radiation of the same wavelength.

Referring to FIG. 4, the relative spectral response of well-cycled plates is graphically illustrated when exposed to illumination having a color temperature of 2800° K. By “relative spectral response” is meant the relative spectral photon intensity of the 2800° K illumination times the quantum (photon) efficiency of the plate and which is plotted as the ordinate while wavelength of the illumination is represented by the abscissa. Curve D represents the selenium test plate of the prior art while Curve E represents the average of the plates of the examples in accordance with the invention. The overall plate speed is proportional to the area under the curve from which it can be seen that substantially plate speed is gained with plates of the invention, particularly in the range of wavelengths between approximately 500 and 700 millimicrons.

Tests for electrical behavior were performed by exposing the charged plates that had been well cycled to a 200 watt incandescent bulb through a range of aperture openings between f/4.5 and f/22. Initial sensitizing charges of negative polarity were applied to the plate of the examples whereas positive polarity charges were applied to selenium plates of the prior art. After exposure the residual potential on each plate was measured. The result of these tests is graphically illustrated by the curves of FIG. 5 in which residual plate potential is plotted as the ordinate and the log exposure of the various openings as the abscissa. Curve F represents a plate in accordance with the invention which has been sensitized with a negative polarity charging potential while curve G represents a commercial selenium plate that was sensitized with positive polarity charging potential.

At the f/11 aperture opening in accordance with the tests of FIG. 5, potential on a plate of the invention was measured before exposure approximately 5 seconds after charging and then measured after exposure with and without regeneration, and the difference in potentials measured being defined as the “electrical contrast.” It was found that regeneration in the instance of a first used plate or after a prolonged rest, or regeneration with a well-cycled plate of several hundred cycles, substantially increased the electrical contrast. Table I tabulates average characteristics of the plates without regeneration while Table II tabulates average characteristics with regeneration. Vp represents the first measured charge while Vc is the contrast potential difference.

<table>
<thead>
<tr>
<th>Table I</th>
<th>No. Cycles</th>
<th>Vp</th>
<th>Vc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2</td>
<td>600</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>670</td>
<td>670</td>
<td></td>
</tr>
<tr>
<td>Several hundred</td>
<td>500</td>
<td>500</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table II</th>
<th>No. Cycles</th>
<th>Vp</th>
<th>Vc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2</td>
<td>670</td>
<td>670</td>
<td></td>
</tr>
<tr>
<td>35-40</td>
<td>690</td>
<td>690</td>
<td></td>
</tr>
<tr>
<td>Several hundred</td>
<td>690</td>
<td>690</td>
<td></td>
</tr>
</tbody>
</table>

After initial completion of the testing, the testing was repeated using duplicated batches of plates constructed similarly in accordance with the examples. These plates were found to be similarly responsive, thus establishing reproducibility with reliability of characteristics. Good results were found with selenium-tellurium layers of about .01 micron thickness to about 1.0 micron thickness. Good results were obtained with selenium-tellurium alloys in which the percent tellurium by weight varied between about 5% and about 40%. Optimum results were obtained with approximately 20-28% tellurium by weight with 25% being preferred. It has been found that the spectral response extends further towards the red as the percentage of tellurium is increased but that dark decay and residual potential increase with tellurium concentrations of over 25% thus reducing the available electrical contrast. Thickness of the selenium storage layer is usually on the order of between 10 and 300 microns.

A protective overcoating was found to preserve the plate characteristics under extended recycling although initially offered no perceptible advantage nor did it in any obvious way enhance the plate properties except to effect preservation. Protective layers other than that disclosed can be used in the alternative as for example an inorganic layer such as disclosed in U.S. Patent 2,866,434.

Regeneration and regeneration were found to improve the electrical contrast characteristics of the plates of the invention although these same plates when operated without regeneration and regeneration produced sufficient electrical contrast for image reproduction.

In addition, a multiplication effect (i.e., quantum efficiency greater than 100%) has been observed in selenium plates according to the invention when sensitized with negative charging. This multiplication effect comes about by placing a transparent conductive electrode extremely close to the surface of the plate rather than in the more conventional charging, exposing, and developing pro-
procedure described herein. It is believed that special procedures as above are necessary for multiplication mechanism in xerographic plates but do not of themselves cause such multiplication.

The reasons for the instant plates achieving the unexpected results of the invention in contrast to prior known plate structures is not fully understood, however, the results may be attributed to the processing or the preparation of the plates as exemplified by the examples.

Selenium alloy plates may be particularly adapted to negative charging yet it has not heretofore been possible to employ negative charging because of the relatively unfavorable properties of the pure selenium storage layer. The special selenium processing is required to make the plates adaptable to negative charging. Very brief processing of the type described has a beneficial effect upon the properties of conventional selenium plates when used with positive charging, but it is believed that the more extensive processing described herein is desirable to impart optimum selenium properties for negative charging.

What is claimed is:

1. An imaging method comprising:
   (a) providing a xerographic plate having an electrical conductive support, a layer of long electron range vitreous selenium overlaying said support, and a layer overlying said vitreous selenium layer comprising a selenium-tellurium alloy containing between about 5 to 40 percent tellurium by weight;
   (b) electrostatically charging said plate to a negative potential;
   (c) exposing said plate to a pattern of light and shadow to form a latent electrostatic image;
   (d) developing the plate with electroscopically attractable material to form an image;
   (e) transferring the image to a support material;
   (f) charging said plate to a positive potential, whereby said plate is regenerated for further use.

2. The method of claim 1 wherein during the positive charging step the plate is exposed to uniform illumination.

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