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3,352,669

PHOTOCONDUCTIVE MEMBER AND PROCESSES OF PREPARING AND USING SAME

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ABSTRACT OF THE DISCLOSURE

A photoconductive member and process of making and using same wherein said member comprises a photoconductive insulating layer overlying an electrically conductive base, the surface of which has been treated with an aqueous mineral acid solution containing chromic acid anhydride or chromic acid in a predominating amount.

This invention relates to electrophotography and more particularly to an improved photoconductive member adapted for use in electrophotography.

In electrophotography, it is known electrostatic images on the surface of a photoconductive insulating layer are produced by uniformly charging the insulating layer and then dissipating this charge on that portion of the layer which is exposed to light. The latent image formed thereon will correspond to the configuration of the light image passing through the master to be reproduced. This image is rendered visible by depositing on the insulating layer a finely divided developing material comprising a colorant called a toner and a toner carrier. The developing material will be attracted to that portion of the layer retaining a charge thereby distributing itself over the layer in a manner corresponding to the electrostatic image. The powder image may then be transformed to paper or other recording surfaces by placing the surface of the paper in contact with the powdered layer and applying an electrostatic charge to the paper. The paper, upon being separated from the insulating layer, will bear the powdered image which may subsequently be made permanent by heating or other suitable fixing means. This above general process is disclosed in detail in United States Patents 2,297,691, 2,357,809, 2,891,011 and 3,079,342. The means supporting the photoconductive insulating material above described usually comprises a metallic or conductive backing member supporting on one surface thereof a barrier layer or interfacial barrier. Over this barrier layer or to form an interfacial barrier, the above mentioned photoconductive electrically insulating material is then deposited. Several suitable processes may be followed to form this photoconductive layer such as, for example, that process disclosed in United States Patent 2,970,906.

A purpose of the barrier in a photoconductive plate of the type described in the above patents is to reduce the charge leakage in the absence of activating radiation (dark discharge) but not preventing the charge dissipation in the presence of such radiation. The barrier also must be designed to prevent or reduce variation in performance of the plate upon reuse or/and recycling of the plate. This variation in performance upon recycling is known as "charge fatigue." Thus, the interface or barrier layer prevents the passage of charge from the conductive backing member to the photoconductive insulating layer and hence prevents discharge of the said photoconductive layer.

Various known materials have been used to form barrier layers. Many, however, have inherent disadvantages making them commercially undesirable. Those, for example, which coat the metallic or conducting surface in a

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non-uniform manner are not suitable since the plate potential will vary as will other properties along the surface. Also, materials reactive with the photoconductive material will, over a period of time, cause a variation in the performance of the photoconductive plate due to changes in the chemical composition thereof. This reactivity has been observed when selenium is used as the photoconductive material. Because of the chemical reaction of the selenium with the barrier layer, non-uniform performance of the electrophotographic process occurred. Another problem encountered is that of adhesion of the photoconductive material to the barrier layers heretofore used. Poor and non-uniform adhesion of the photoconductive layer to the barrier layer leads to plate failure by element separation in use.

It is therefore an object of this invention to provide a barrier member for supporting the photoconductive material of an electrophotographic plate which is devoid of the above noted disadvantages.

Another object of this invention is to provide an improved electrophotographic plate comprising a novel barrier layer which will substantially minimize "dark discharge" and "charge fatigue."

Another object is to provide a novel method for the production of an electrophotographic plate.

Still another object of this invention is to provide a barrier layer which will reduce significantly any chemical reaction with the photoconductive material.

Another still further object of this invention is to provide a barrier layer for use in an electrophotographic plate which will maintain at a minimum the variation of properties in the photoconductive material during use.

Yet another still further object of this invention is to provide an electrophotographic plate which performs in a substantially consistent manner upon reuse.

A further object of this invention is to provide an electrophotographic plate having desirable adhesion of the photoconductor to the barrier layer.

The foregoing objects and others which will become apparent from the following description are accomplished in accordance with this invention, generally speaking, by providing a photoconductive member comprising a barrier layer obtained by contacting an aqueous mineral acid solution containing chromic acid anhydride (CrO_3) or chromic acid (H_2CrO_4) in a predominating amount, with a conductive supporting substrate. In place of, or together with the CrO_3 or H_2CrO_4 , it is intended that the water soluble salts of these materials may be utilized. Typical water soluble salts are: potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$, ammonium dichromate (NH_4) $_2\text{Cr}_2\text{O}_7$, and mixtures thereof. By predominating amount, for the purposes of this disclosure, is meant in an amount by weight of at least about 50% of the solute used in said acidic water solvent, to about 100%. The supporting substrate may be of several desirable conductive materials such as aluminum, copper, nickel, magnesium, tin, zinc, cadmium, silver, ferrous material, their alloys and mixtures thereof. The preferred supporting substrate is a brass material having from about 60% to about 95% copper and the remainder zinc. In the solution containing chromic acid anhydride or/and chromic acid and/or their water soluble salts, a chromate conversion activator is normally used. Any suitable activator may be used such as, for example, zinc chloride, halogenated mineral acids, alkali metal chlorides, acid soluble bromides, thiocyanates, thiosulfates, iodates, fluorides, arsenates, acetates and mixtures thereof. Specific suitable activators are potassium bromide, potassium iodate, sodium thiocyanate, sodium thiosulfate, hydrochloric acid, hydrobromic acid, ammonium bromide, sodium bromide, zinc bromide, zinc chloride, sodium sulfite, sodium

sulfate, sodium acetate and mixtures thereof. It has been considered, however, that the activator may promote oxidation-reduction reactions between the metal surface to be treated and the particular chromium compound present in the solution. It has been further considered that the activators cause formation of a chromic compound at the surface of the metal forming thereon a chromate type surface or layer. Any suitable photoconductive layer or material may be used such as amorphous selenium, zinc oxide, zinc-cadmium sulfide, tetragonal lead monoxide, titanium dioxide and mixtures thereof. The barrier layer thickness may be controlled to obtain desirable properties or optimum combinations of desirable properties depending on the material of the supporting substrate, the formulation, concentration and other materials used and functional needs, etc. The CrO_3 or H_2CrO_4 can be used in an acid medium such as, for example, H_3PO_4 , HCl_3 , HNO_3 , H_2SO_4 , and mixtures thereof.

In a preferred embodiment of this invention, a barrier layer having a thickness of up to about one-half micron is formed by contacting the surface of the conductive supporting substrate with an aqueous nitric acid solution containing the CrO_3 or H_2CrO_4 moiety. The proportions of this material, of course, will vary depending upon the particular desired result; however, it is preferred that an acid solution containing nitric acid and a composition comprising from about 80% to 95% CrO_3 and from about 5% to 15% Na_2SO_4 be used. It is considered also that commercial grade materials may be used which, of course, will contain a number of minor impurities, none of which are known to have any appreciable effect upon the desired barrier layer.

The following examples will further define the process, plate and barrier layer of this invention. Parts and percentages are by weight unless otherwise indicated. The examples below also specifically illustrate various preferred embodiments of the present invention.

Example I

A chromic acid solution from which the barrier layer is formed is prepared by mixing for each gallon of water about two ounces of a composition containing about 6% Na_2SO_4 , about 90% CrO_3 , about 2% $\text{Cr}_2(\text{SO}_4)_3$ and the remainder various substantially insignificant impurities.

A brass support or supporting substrate having a composition of about 70% copper and about 30% zinc is used in the form of a brass foil, or a brass plate, or a brass drum. All of these brass supports can be used and will function in substantially the same manner. The brass support is immersed in the aqueous working chromic acid solution above defined. The solution is maintained at a temperature of about 100° F. while the support is immersed for a period of about twenty seconds. Upon removing, the treated support is rinsed for a period of about sixty seconds with water at a temperature of about 100° F. The rinsing is followed by two cold tap water rinses and then a cold deionized water rinse, all about fifteen seconds each. The treated support is then dried for about fifteen minutes at a temperature of about 100° F. This forms a barrier layer on the support. The treated support is then placed in a high vacuum evaporator where selenium is deposited on the support by known vacuum evaporation methods such as that described in U.S. Patent 2,970,906. Other known methods to deposit the selenium may also be used. For example, in one method used, the selenium coating is accomplished by conducting vaporized selenium from a body of selenium to a plate in an upwardly directed path for approximately ten minutes while maintaining the treated support at a temperature of from about 100° C. to about 120° C. Other suitable selenium deposition methods such as spraying and hot pressing suitable for use in the present process are disclosed in the above noted patent U.S. 2,970,906. A selenium layer of about 40 microns is thereby formed over the barrier layer to provide the finished xerographic plate.

Example II

A working solution is prepared by admixing one gallon of water with one ounce of a composition containing about 13% Na_2SO_4 and about 86% CrO_3 , and about 12 ml. of a concentrated nitric acid (40° Bé.).

Into this solution the brass supporting substrate is immersed in a manner similar to that described in Example I. The support is immersed while maintaining the solution at a temperature of from about 85° F. to about 145° F. The support is maintained in the solution for a period of about ten to sixty seconds and then upon removing is rinsed with water in the same manner as indicated above in Example I. The treated support is then dried for a period of about ten to twenty-five minutes at a temperature of about 85° F. to about 145° F. and coated with selenium by the method disclosed in Example I. The photoconductive plate produced has a barrier layer over the brass support and has coated thereon a selenium layer ranging from about 20 to 80 microns.

Example III

Various chromic acid solutions are formulated by mixing with one gallon of water from about two to about sixteen ounces of a material containing about 90% CrO_3 , about 2% $\text{Cr}_2(\text{SO}_4)_3$, about 6% Na_2SO_4 , and the remainder various substantially insignificant impurities. The process using each of the solutions formulated is as follows:

A brass support having a composition of about 70% copper and about 30% zinc and in the form of a foil, plate or drum, is immersed in the solution as above indicated. The brass support is maintained in the solution for a period of about ten to thirty seconds at a temperature of from about 85° F. to about 145° F. The support is then removed from the working solution and rinsed with water at a temperature of from about 85° F. to about 145° F. for a period of about thirty to ninety seconds. The support is then further rinsed by cold tap water and subsequently a cold deionized water rinse, each rinse conducted from about ten to about twenty-five seconds. The treated support is then dried for about ten to about twenty-five minutes at a temperature of about 100° F. to about 145° F. The selenium coating is then deposited thereon in a manner similar to that discussed in the above Examples I and II.

Example IV

The working solution described in Example I is deposited in a suitable containing vessel and a continuous brass foil strip is passed therethrough. Prior to entering the vessel containing the chromic acid solution, the foil will pass through a trichloroethylene vapor degreaser. After the foil has passed through the chromic acid solution, it is fed through a hot water rinse tank, two-spray cold water rinsing means, a cold deionized spray rinsing means, and then through a drying oven. The brass strip is then re-rolled on a take-up spool and is ready for selenium deposition.

In a specific procedure the brass foil strip is passed through the chromic acid, rinsing and drying vessels at a rate of about six feet per minute. The specific chromic acid working solution contains about eight ounces of a composition containing about 7% Na_2SO_4 , 91% CrO_3 , and about 2% $\text{Cr}_2(\text{SO}_4)_3$ per gallon of water. The temperature of this solution is kept at about 100° F. and the foil maintained in the solution for a period of about thirty-five seconds. The hot water rinse is adjusted to a temperature of about 100° F., the oven is maintained at a temperature of about 170° F. and the foil remains in the oven for approximately one and one-half minutes. The foil from the take-up spool is then transported to a high vacuum evaporator where selenium is deposited on the foil by any known method, for example, one described in United States Patent 2,970,906. The final photoconductive plate prepared has a barrier layer with a selenium photoconductive layer of about 60 microns thickness.

It should be understood that any of the above materials considered as suitable for use as the conductive supporting substrate, photoconductive material and ingredients in the barrier layer forming solution, can be substituted in the above examples for the specific materials set forth therein.

Although the invention has been described in considerable detail, the foregoing examples were used only for the purpose of illustration. It should be understood that such detail is solely for the purpose of illustration and not limitation. Those skilled in the art, upon reading the foregoing discussion, will conceive of other modifications, and ramifications of this invention; these are intended to be encompassed within the present invention.

What is claimed is:

1. A photoconductive member comprising an electrically conductive supporting substrate, a barrier layer in electro-chemical contact with and directly overlying at least a portion of said supporting substrate, and a substantially vitreous photoconductive insulating layer comprising amorphous selenium substantially permanently affixed to said barrier layer, said barrier layer obtained by contacting said supporting substrate with an aqueous mineral acid solution comprising a member selected from the group consisting of H_2CrO_4 , CrO_3 , their water soluble salts, and mixtures thereof.

2. A photoconductive member according to claim 1 wherein said supporting substrate comprises from about 5% to about 40% zinc and the remainder copper.

3. The process for the production of a photoconductive plate adapted for use in electrophotography which comprises contacting a mineral acid solution of a member selected from the group consisting of CrO_3 , H_2CrO_4 , their water soluble salts and mixtures thereof; and about 0.10% to about 15% Na_2SO_4 based on the total weight of the solute used, with an electrically conductive metallic supporting substrate comprising from about 5% to about 40% zinc and the remainder copper to form thereon a barrier layer, said acid solution contacted with said electrically conductive supporting substrate until a barrier layer having a thickness of from about 0.0005 to about 2.0 microns is formed thereon, and subsequently depositing over at least a portion of said barrier layer a substantially vitreous photoconductive insulating material comprising amorphous selenium.

4. The process for the production of a photoconductive plate adapted for use in electrophotography which comprises contacting a nitric acid solution of about 80% to about 95% CrO_3 and from about 5% to about 15% Na_2SO_4 , based on the total weight of the solute used, with an electrically conductive metallic supporting substrate comprising from about 5% to about 40% zinc and the remainder copper to form thereon a barrier layer, said acid solution contacted with said electrically conductive supporting substrate until a barrier layer having a thickness not greater than about 0.5 micron is formed thereon, and subsequently depositing over at least a portion of said barrier layer a substantially vitreous photoconductive insulating material comprising amorphous selenium.

5. The process for the production of a photoconductive plate adapted for use in electrophotography which comprises contacting a mineral acid solution comprising nitric acid and a solute comprising CrO_3 in an amount of from about 50% to about 95% based on the total weight of the solute and the remainder of said solute a chromate conversion activator, with an electrically conductive metallic supporting substrate comprising from about 5% to about 40% zinc and the remainder copper to form thereon a barrier layer, and subsequently depositing over at least a portion of said barrier layer a substantially vitreous photoconductive insulating material comprising amorphous selenium.

6. The process for the production of a photoconductive plate adapted for use in electrophotography which comprises the successive steps of:

(a) contacting a brass substrate comprising from about 5% to about 40% zinc and the remainder copper to a mineral acid solution comprising a member selected from the group consisting of H_2CrO_4 , CrO_3 , their water soluble salts and mixtures thereof, the solution at a temperature of from about 85° F. to about 145° F. and the duration of the contact being between about 10 and about 60 seconds; and,

(b) depositing over at least a portion of said treated brass substrate, a substantially vitreous photoconductive insulating material comprising amorphous selenium.

7. An electrophotographic process wherein the photoconductive member of claim 1 is provided with a latent electrostatic image and developed with electrically tractable marking particles.

8. An electrophotographic process according to claim 7 wherein the latent electrostatic image is provided by electrically charging said member and then exposing the charged member to a light image pattern to be reproduced.

9. An electrophotographic process wherein the photoconductive member of claim 2 is provided with a latent electrostatic image and developed with electrically tractable marking particles.

10. An electrophotographic process according to claim 9 wherein the latent electrostatic image is provided by electrically charging said member and then exposing the charged member to a light image pattern to be reproduced.

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