

[54] **GLOW DISCHARGE TECHNIQUE FOR THE PREPARATION OF ELECTROPHOTOGRAPHIC PLATES**

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Related U.S. Application Data

- [62] Division of Ser. No. 39,945, May 20, 1970, abandoned.
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[58] Field of Search. 117/106 A, 213, 69; 204/164

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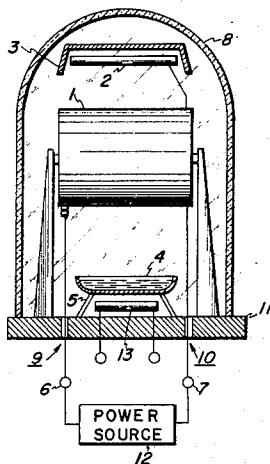
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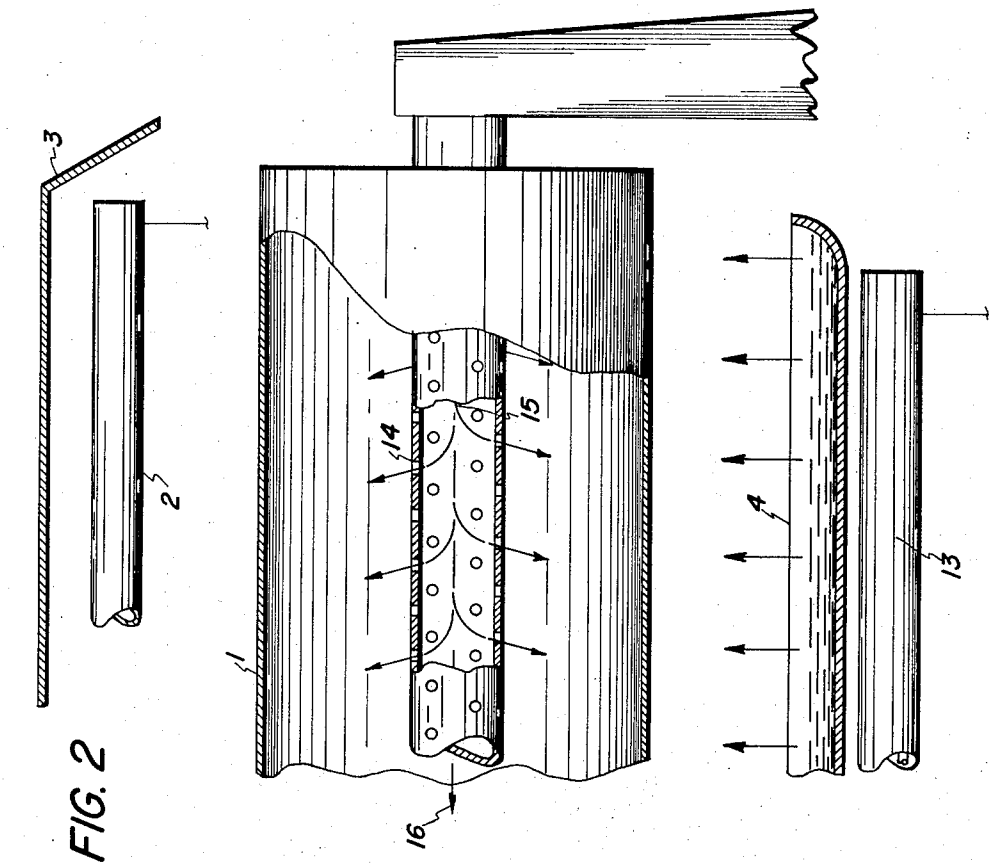
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[57] **ABSTRACT**

A method of preparing an electrophotographic plate having a metallic oxide coating interface is disclosed. The preparation of the plate involves subjecting a metallic substrate to a glow discharge process by utilizing it as the anode electrode in the electrical discharge process. The glow discharge effects oxidation of the surface as well as heating the substrate to a temperature at which vacuum evaporation of the photoconductive layer takes place. The process has particular utility because the glow discharge — oxidation process effectively cleans the metallic substrate thereby preparing it for the subsequent evaporation of a pure photoconductive material such as selenium.

4 Claims, 2 Drawing Figures





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GLOW DISCHARGE TECHNIQUE FOR THE PREPARATION OF ELECTROPHOTOGRAPHIC PLATES

This is a division of application Ser. No. 39,945, filed May 20, 1970 now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to a method of employing current to form films upon the surface of a metal by employing such metal as an electrode in a glow discharge reactor. More specifically, the invention relates to an improved coating technique employing glow discharge in the preparation of xerographic plates.

The various phenomena of gaseous electrical discharges have been the subject of continuing investigation from the last part of the 19th century to the present time. Generally, these are referred to as non-self maintaining discharge, breakdown discharge, self sustaining discharge, corona and brush discharge, glow discharge, and arc discharge; in order of increasing current flow. Another term employed for several types of these discharges is mentioned as "silent discharge." Throughout the studies on these discharges various gaseous substances have been used to sustain the ionization effects of the potential necessary to cause the discharge to occur.

While many of the different types of electrical discharges have been reported in the early art, the more recent art has been particularly concentrated upon the glow discharge. This type of discharge occurs at low pressures and only over a rather narrow range of glow current densities between the electrode surfaces. In line with the undesirability of disruptive type discharges such as arcing discharges, the recent art has proposed to limit the current causing the glow discharge to prevent such arc.

The present invention relates to the use of glow discharge in the preparation of electrophotographic plates. According to present technique in the preparation of electrophotographic plates, metallic substrates, such as aluminum, are passed through a series of cleaning processes prior to deposition of the photoconductive layer. In this cleaning process generally the metallic substrate is passed through a series of chemical cleaning tanks containing alkaline and/or acidic substances which effectively clean the surface by etching. After the cleaning process the substrate is then dried and subsequently placed in a high temperature furnace where it is subjected to a temperature of over 200°C for approximately 30 minutes in order to form an oxide layer thereon. The substrate containing the oxide layer is then placed in a vacuum evaporation chamber wherein the photoconductive layer is vacuum evaporated thereon and there results a xerographic plate having a substrate, an interface layer of metallic oxide, and a photoreceptor layer.

While the aforementioned method results in satisfactory electrophotographic plates there are several distinct and significant disadvantages to such a process. First, the process requires a series of steps which are physically independent from one another and therefore are obviously time consuming. Secondly, the physical transfer of the substrate subjects it to handling which increases the risk of contamination. Thirdly, the oxidation step in the high temperature oven takes place under atmospheric conditions and therefore there is

additional risk of contaminants and impurities adhering to said substrate during the oxidation.

According to the present invention, it has been found that electrophotographic plates can be prepared by a glow discharge technique in combination with an evaporation process. By means of this process it is possible to produce electrophotographic plates having uniform metallic oxide interfaces thereby resulting in plates having excellent dark discharge characteristics, i.e., plates having low dark decay. Homogeneity and uniformity of the metallic oxide interlayer are advantageous in electrophotography because of the strict physical and electrical parameters that are imposed in high quality imaging and recording.

In the most general practice of the present invention the metallic substrate is used as a discharge electrode in a glow discharge process. More specifically, the metallic substrate is grounded as the anode electrode in a vacuum system and upon the application of current the glow discharge between the cathode and the substrate sets up a plasma state such that the ionized air in the vacuum system bombards the metallic anode resulting in surface oxidation as well as heating of the substrate. When necessary, the substrate is then cooled to an appropriate temperature at which vacuum evaporation takes place.

OBJECTS OF THE INVENTION

It is therefore an object of this invention to provide an improved method and apparatus for producing highly uniform films on substrates which overcome the above-noted disadvantages.

It is yet another object of this invention to provide a method and apparatus for producing highly uniform photoconductive films and interfaces contained on a substrate.

It is another object of this invention to provide a method of forming improved imaging members for electrophotography.

It is yet another object of this invention to provide a preparation of an improved interface for electrophotographic plates.

BRIEF SUMMARY OF THE INVENTION

The foregoing objects and others are accomplished in accordance with this invention by providing a method and apparatus for coating an electrophotographic substrate which comprises subjecting a metallic substrate surface to glow discharge in a vacuum environment whereby the metal is heated and a metallic oxide formed on the surface of the substrate and thereafter vacuum evaporating a layer of photoconductive material onto said substrate.

The use of glow discharge in the preparation of electrophotographic plates essentially accomplishes three important functions ordinarily required in the vacuum evaporation of photoconductive coatings on electrophotographic plates. In the first instance the electrical discharge heats the drum thereby preparing it for vacuum evaporation. Secondly, the discharge causes bombardment of the anode substrate with ionized oxygen molecules which oxidize the surface to produce a metallic oxide layer. Thirdly, in oxidizing the surface the glow discharge effectively oxidizes any possible contaminants and thereby cleans the surface of the metal anode.

For purposes of illustration, and one embodiment of this invention, an aluminum drum is placed in a coating chamber at positive ground potential. The coating chamber also contains a spaced cathode and an evaporation source containing pure selenium. The chamber is then evacuated to a sub-atmospheric pressure and power is applied between the cathode and substrate using a D.C. discharge. The resulting electrical discharge is continued for a time sufficient to cause a formation of a desired thickness of amorphous aluminum oxide on the surface of the drum. After the electrical discharge is suspended the drum, which has been heated during the electrical discharge, is cooled, if necessary, to a suitable temperature and vacuum evaporation of the pure selenium onto the drum is then initiated. There results from this process a xerographic drum having an aluminum substrate, an amorphous aluminum oxide interface layer, and an amorphous selenium photoconductive layer.

This novel method is particularly adapted to the vacuum evaporation of photoconductor materials and may be used in the preparation of binder or layered photo-receptors. The photoconductor materials include selenium, arsenic, tellurium, antimony, bismuth, thallium, sulfur, and mixtures, and alloys, thereof. It should be understood that the photoconductor materials may contain small amounts of certain additives which modify or enhance electrical or physical properties. For example, materials such as halogens, which include iodine, chlorine, fluorine and bromine, may be added to arsenic-selenium alloys in order to increase the sensitivity of this alloy. In addition to the photoconductor materials mentioned above, organic photoconductors which can be vacuum evaporated are considered within the purview of the present invention.

In order to attain electrical discharge in the present invention a direct current of from about 100 to 1,000 milliamperes is preferred. The use of an alternating current would result in a reversal of polarity of the electrodes thereby resulting in a partial frustration of the oxidation process at the surface of the metallic substrate. A voltage of from about 1,000 to 10,000 volts is required in order to obtain sufficient power. It is found that within these electrical parameters effective glow discharge takes place.

In another, more specific, illustration of the instant invention, an aluminum drum substrate is inserted as the positive potential electrode, the anode, in a glass Bell jar vacuum coater. A glow discharge cathode and shielding was installed above the drum, the shielding being used to protect this glass. A two cavity open boat crucible containing substantially pure selenium is then placed beneath the drum. A variac glow discharge power supply, Model 922-002 is used as a high voltage power source. A needle valve is installed to regulate the Bell jar pressure at any desired level.

The system is then evacuated to a pressure of about 40 microns of Hg and the needle valve cracked until a pressure of 40 microns of Hg is sustained. A glow discharge is then effected by application of the power source at voltage of about 5,500 volts. The glow discharge continues for about 3 minutes which raises the temperature of the drum from about 23°C to about 50°C. At this point the selenium crucible is heated to about 220°C by means of a resistant heating element and evaporation of the selenium on the drum is allowed to take place for an 18 minute period. There results a

selenium electrophotographic plate having an aluminum oxide interface. The advantages of this improved technique and apparatus will become apparent upon consideration of the following disclosure especially when taken in conjunction with the accompanying drawings wherein:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates a vacuum coating jar, and apparatus for a glow discharge system according to the present invention.

FIG. 2 is another embodiment of a coating apparatus according to the present invention.

DETAILED DESCRIPTION OF THE DRAWINGS

FIG. 1 schematically illustrates a glow discharge coating system for producing coatings in accordance with the present invention. Reaction chamber 8 of FIG. 1 can be any material capable of enclosing a vacuum chamber including such materials such as glass or quartz, metals, etc. The reaction chamber includes an inlet port 9, and an outlet port 10, for connection to an evacuation system.

The pair of electrical leads 6 and 7 are shown passing up through the undersurface of plate 11, one being in contact with a high voltage cathode, 2, surrounded by a shielding device, 3, and the other being in contact with the metallic substrate, which functions as the anode and is shown in the figure in a drum configuration designated as 1. These leads are connected to a high voltage power source 12 which can be operated at constant amperage.

The apparatus also includes one or more pedestals represented at 5, each of which is provided with a heater represented at 13. The evaporation crucible containing the photoconductor material to be evaporated onto the metallic substrate is designated as 4.

In actual operation, the pressure in the coating apparatus of FIG. 1 is reduced to below 200 microns of mercury. A sufficiently high voltage is then applied from the high voltage power source, 12, to cause the discharge between the cathode, 2, and the metallic drum anode thereby forming a glow discharge throughout the chamber. As the pressure is further reduced to below 100 microns of mercury, the glow discharge becomes crossed by a series of dark zones assuming the form of the classical glow discharge. In front of the cathode is a glow termed Cathode glow, followed by a dark space called the cathode or Crooke's dark space. The cathode dark space is followed by another glow called the negative glow, which is the most luminous of all the glows. This is followed by the Faraday dark space, and a long glowing region known as the positive column. Further reduction in the gas pressure will cause the cathode dark space to expand at the expense of the positive column, and when a pressure of the order of 15 microns of mercury is reached, the cathode dark space will increase significantly in length. Should the cathode dark space expand sufficiently to contact the anode electrode the discharge is extinguished.

For the maintenance of a glow discharge from the cathode electrode, 2, there must be a definite relationship between the number of electrons ejected from the cathode per positive ion compact and the number of positive ions produced by electrons colliding with gas molecules, i.e., for the discharge to be maintained an electron must in its passage, through the atmosphere

remaining in the apparatus, produce that number of positive ions which upon striking the cathode will release a new electron.

DESCRIPTION OF SPECIFIC EMBODIMENTS

In terms of a specific embodiment of this invention as illustrated by FIG. 1, an aluminum drum being approximately $4\frac{1}{2}$ inches in diameter and 12 inches wide in size and normally used in a Xerox 813 machine is mounted on a rotating means as the anode substrate 1 in the vacuum coater of FIG. 1 and set rotating at about 6 revolutions per minute. Inlet port, 9, is sealed off and outlet port, 10, is connected to a vacuum pump which is operated to reduce the pressure inside the chamber 8 from atmospheric pressure to about 15 to 200 microns of mercury. A Varian glow discharge power supply, Model 922-0002, was used as a high voltage power source, 12, and set at maximum power. A voltage of from about 5 to 10 kilovolts is applied depending upon the pressure within the coating chamber. The application of the voltage results in a glow discharge occurring within the evacuated coater and said discharge effectively causes the rotating anode aluminum drum substrate to be exposed to ion bombardment. The discharge is continued for a time necessary to effect a sufficient uniform formation of amorphous aluminum oxide over the whole drum surface which layer will ultimately function as an interface in a xerographic drum. Generally the exposure time corresponds to the time required to attain a substrate temperature at which vacuum evaporation of the photoconductor material can take place.

The glow discharge is then terminated and either the drum is allowed to cool to a temperature at which vacuum evaporation takes place or, should the drum be at the appropriate temperature at the end of the glow discharge, vacuum evaporation takes place immediately. When the drum has reached a suitable evaporation temperature the crucible containing substantially pure selenium is heated by means of the heating element 13. Deposition of the selenium on the aluminum oxide coated substrate 1 then takes place in an evaporation cycle of less than 20 minutes, the final photoreceptor layer being about 60 microns. It should be understood, however, that the rate of deposition for evaporation for any of the aforementioned steps may be increased or decreased by simply varying the process parameters by techniques well known in the art.

While describing one operation of the instant invention in terms of the glow discharge oxide formation and cooling of the drum as being sequential steps, the practical aspects of the instant invention do not dictate such an order. Therefore because metallic oxide interface layers to be effective only have to be from about 15 to 55 angstroms thick the glow discharge is generally continued until the metal substrate is raised to the temperature at which the vacuum evaporation of the photoreceptor material is to take place. More specifically, the time of glow discharge is limited only insofar as restricting the amount of heat generated by the power being put into the system. Although this period of discharge will differ depending upon the particular material to be evaporated, the discharge time will be sufficient to form an oxide layer within the thicknesses recited above.

The operating pressure of the above described process may be selected within the range of from about 15

microns of mercury to several hundred microns of mercury, depending upon the voltage and current supplied from the power source. However since the instant process is concerned with the formation of the metallic oxide interface on the metallic substrate during the glow discharge process, suitable oxygen is found present at pressures of from about 15 to about 200 microns of mercury. In terms of the time necessary to heat a substrate to a given temperature, optimum conditions are found at pressures of from about 30 to 50 microns of Hg.

As pointed out above, the temperature of the substrate will depend upon the particular material or alloy to be deposited. Generally substrate temperatures will range from about 40°C to 400°C depending upon the material to be evaporated. If the photoreceptor material is thought to be in the amorphous form these temperatures are sufficient.

In the practice of the present invention with respect to the use of glow discharge to form oxide coatings on metallic drum substrates it is possible to use a universal coater. As illustrated in FIG. 2, in carrying out the coating of a drum surface by glow discharge in a vacuum coater, a universal mandrel 13 could be used not only as a support core during coating but also as a means for cooling said drum surface after the ion bombardment and evaporation processes. The mandrel will be a length of pipe, the diameter of which would be smaller than that of the particular drum being coated. The mandrel would be used as a means for cooling the drum after glow discharge process and also after the evaporation cycle by means of introducing dry nitrogen or air through the hollow core of the mandrel and into the coating chamber. This can be more graphically seen by reference to FIG. 2 where the mandrel designated 14 is shown as a hollow cylindrical core with a perforated surface. The inlet designated as 15 in the figure is that point which air or dry nitrogen is injected for purposes of drum cooling. The gas then proceeds along the length of the mandrel and seeps through the perforated holes of the perforated cylinder indicated by the arrows to reach the underside of the heated drum. In this manner a means is provided for regulating the temperature of the drum surface both after glow discharge and after evaporation thereby facilitating the coating process in terms of efficiency and time.

In the actual operation of this embodiment of the invention a potential is applied between the anodic drum 1 and the high voltage cathode designation as 2 thereby resulting in a glow discharge between the two electrodes. The discharge is continued for time sufficient to cause a formation of metallic oxide on the surface of said drum said coating being capable of functioning as an interface layer in a xerographic photoreceptor. Upon termination of the glow discharge, air is pumped through the inlet 15 where it links the vacuum and circulates through the mandrel and reaching the under-surface of the heated drum by way of the perforated holes in the cylindrical core, the excess air being pumped through the perforated mandrel that exits at the outlet designated as 16. The cooling air then reduces the temperature of the metallic drum substrate to a point at which vacuum evaporation of pure selenium, located in the crucible designated as 4, can be vacuum evaporation thereon. The system is then evacuated again and the crucible 4 is heated and the drum 1 is carried through an evaporation cycle after which

air is again circulated through the perforated mandrel for purposes of cooling the drum or purposes of removal from the coating apparatus.

Operation of the apparatus as well as the various electrical and physical parameters illustrated in FIG. 2 is essentially the same as described in connection with FIG. 1. An appropriate vacuum system evacuates the coating apparatus by means of an exit port as in 10 of FIG. 1. The drum anode and cathode are electrodes in the same manner as illustrated by 6 and 7 of FIG. 1.

layer is again measured and the values recorded. As can be seen from the results outlined in Table I in each run there is significant increase in the oxide barrier units which can only be attributed to the glow discharge process which additionally forms aluminum oxide on the surface of the 813 drum. It is to be further noted that runs three and four illustrate optimum pressures of from about 30 to 50 microns of Hg at which to achieve a given substrate temperature in the shortest time using approximately the same power.

TABLE I

	Pressure in of Hg	Exposure Time In Minutes	Voltage In Volts	Current in AMPS	Initial temp °C	Final temp °C	Initial Oxide Barrier Units (OBU)	Final Oxide Barrier Units (OBU)
1	100	5	1080	0.3	23°	120°C	9.0	30.1
2	45	10	4500	0.44	23°	175°C	13.4	34.2
3	50	5	5300	0.36	23°	85°C	9.6	27.6
4	45	2	4400	0.46	23°	85°C	9.2	16.4
5	42	3	5600	0.26	23°	75°C		

The photoreceptor material is heated by a heating element such as 13 and FIG. 1 and the material evaporated in the direction of the substrate on which it forms a highly uniform adherent coating.

The following examples of practice are meant to be descriptive of various manners of which the method of this invention may be used to produce the interface and photoreceptor coatings according to the present invention. The examples of practice are not intended to be limitative of the invention.

EXAMPLE I

Four runs were made at the electrical parameters set out in the first four runs in Table I below. The operating procedure is as follows: An 18 inch pilot coater is outfitted with a hand build cylindrical rotating fixture, such as that shown in FIG. 2, for an 813 size aluminum drum. A glow discharge cathode and shielding was installed about 5 inches above the drum and a 2 cavity open boat crucible was installed beneath the drum as shown in FIG. 2 at a distance of about 1 inch. A Varian glow discharge power supply, Model 922-0002, was used for the high voltage source and a needle valve was installed to regulate the Bell jar pressure at any desired level. The temperature measurement of the aluminum substrate is accomplished with the use of a thermocouple attached to the underside of the drum.

In each of the first four runs set forth in Table I initial oxide barrier units were measured by the standard method utilizing a Hewlett Packard X-Y-Recorder. It is to be noted that the measurement of the oxide barrier units causes contamination of the substrate surface thereby precluding the evaporation of pure selenium, or selenium alloys, onto said contaminated surface. As to be demonstrated hereinafter, when a photoreceptor layer is to be applied the oxide barrier unit cannot be measured (See Example II).

The Bell jar was then evacuated by means of a diffusion pump to about 8 microns of mercury and the needle valve cracked to raise the pressure to the respective pressures listed in Table I. Each of the four 813 aluminum drums were then subjected to a glow discharge of between 2 and 10 minutes depending on the various electrical parameters involved. After the drums were cooled to room temperature by means of the perforated universal mandrel set forth in FIG. 2, the barrier

EXAMPLE II

A fifth drum which is designated as run number 5 in Table I, was also processed by a glow discharge similar to that used on the first four aluminum drums of Example I using the electrical and physical parameters set forth in Table I. There was no measurement of the oxide barrier units because of the contamination factor mentioned above. The glow discharge was continued for a three minute period until the temperature of the drum reached 75°C. The drum was then subjected to an 18 minute evaporation cycle for a selenium alloy mixture having the composition of 99 percent selenium and 1.0 percent arsenic, mechanically mixed with a 30 part per million chlorine doped selenium. The resulting photoreceptor drum was cooled and removed from the coater and plated in an in line 813 scanner where it is electrically scanned. The drum is cycled (charged and exposed) 20 times and the charge fatigue is measured. Contrast potential, residual charge, and dark discharge are then measured sequentially in four cycle modes for each measurement. The results are outlined in Table II.

TABLE II

Initial charge	800 V
Contrast potential	730 V
Residual charge	10 V
Overall dark discharge	150 V
Localized dark discharge	15 V
Charge fatigue	Zero V

The residual charge and charge fatigue values indicate that the interface aluminum oxide layer prepared by the instant glow discharge process acts as an effective barrier layer while not causing excessive charge buildup. It therefore can be concluded photoreceptors having metallic oxide interfaces and prepared by the glow discharge and vacuum evaporation coating process of the instant invention have excellent dark discharge properties.

Without intending to limit the present invention by proposing a theory of operation for the glow discharge process described herein, it is speculated that when a high voltage discharge is passed between the metal electrodes in the evacuated system, there is an initial lowering gas pressure as some of the bombarded gase-

ous molecules are rapidly converted to the solid oxide at the surface of the anode which is under ion bombardment. The reduction in the gas pressure in the evacuated coater is due to the conversion of the ionized gas molecules to the metallic oxide; that is, the rapid flow of electrons from the high voltage cathode ionizes the gaseous molecules of oxygen either in or about the metallic substrate thereby effecting its chemical reaction with the metal. Put another way the rapid release of electrons at the cathode causes a bombardment of the gases in the chamber which results in ionized gases between the cathode and the anodic metallic substrate. The ion bombardment on the metallic substrate then causes oxidation of the substrate surface. In the instance where the aluminum substrate is used the glow discharge causes formation of an amorphous aluminum oxide layer which has excellent characteristics as an interface layer in a xerographic photoreceptor.

All specific components and proportions have been stated in the above description of the preferred embodiments of this invention. Other suitable materials and procedures such as those listed above may be used with similar results. In addition, other means may be used by one skilled in the art which in no way should be construed or restrictive of the scope and spirit of the present invention.

What is claimed is:

1. The process for the preparation of an electropho-

tographic plate comprising:

- a. placing an aluminum substrate as the anode in a pressure coating chamber with a glow discharge cathode,
 - b. reducing the pressure in said coating chamber to between 15 and 20 microns, and applying a glow discharge of from about 1,000 to 10,000 volts and about 100 to 1,000 milliamps between the cathode and the anode,
 - c. continuing said glow discharge for a time sufficient to oxidize said metallic substrate and form a layer of metallic oxide, and
 - d. thereafter vacuum evaporating a photoconductive material on the metal oxide substrate in said chamber.
2. The process of claim 1 wherein the glow discharge is continued for a time sufficient to form a metallic oxide layer of between about 15 and about 55 angstroms.
3. The process of claim 1 in which the glow discharge is carried out at pressures of from about 30 to 50 microns of Hg to effect a formation of amorphous aluminum oxide having a thickness of from about 10 to 55 angstroms.
4. The process of claim 1 in which the photoconductive material comprises selenium and selenium alloys.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,816,288 Dated June 11, 1974

Inventor(s) George S. Lubicz and Alan J. Bills

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, Assignee:, change "Zerex" to --Xerox--.

Signed and sealed this 1st day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents